ASPECTS OF RIVER POLLUTION
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There must be very few people in this country so well qualified as Dr Klein to write a book on 'Aspects of River Pollution'. For nearly twelve years he was research chemist in the Manchester Corporation Rivers Department, where he worked on some of the many problems which arise in the treatment of sewage in a highly industrial area. He has been chief chemist with the old Lancashire Rivers Board and is now chief chemist with the Mersey River Board—an organization serving a district where an unusually wide range of aspects of pollution may be studied within a convenient distance of the laboratory. This first-hand acquaintance with polluting discharges, and with the methods which can in practice be used to purify them—bearing in mind that limitations of space, of skilled supervision, and of finance, together often determine whether a technically possible process is 'reasonably practicable' or not—is very obvious in the book which he has now written. It is being published at a time when there is much discussion on the way in which a river board can best manage the streams for which it is responsible—whether for example it should attempt to apply uniform standards of quality to all the effluents discharged in one district or whether it is better to consider each discharge separately—and on this and similar matters Dr. Klein, with his long experience, speaks with great authority.

But besides making available his own observations and thoughts on pollution, Dr Klein has rendered a tremendous service to everybody interested in this matter by surveying critically the widely scattered and now very extensive literature on the subject—he has included in his book references to more than 1,300 original papers, which means that he must have considered and rejected many times this number. Anybody who has tried to make such a search, even for the purpose of writing a review of developments during a single year or within a narrow field, will know how much labour it has involved. There are times when, surveying the great mass of papers now published and pondering on the wide differences in quality between the best and the worst of them, one fears that the system of communicating scientific information will break down of its own weight. When an expert in his field—and it requires one with unusual patience and fortitude—undertakes to bring such an unwieldy mass of material into order, and to present what is worth keeping in an assimilable form, he renders a very high service to his
fellow workers. This Dr Klein has done, and I know that the by now large number of chemists, engineers and biologists, who deal with problems of pollution and their prevention, will find this book to be of the first importance and of the greatest assistance to them in their work.

B. A. Southgate
PREFACE

It is with some diffidence that I venture to add to the already large number of books on sanitation and public health. 'Of making many books there is no end; and much study is a weariness of the flesh' writes Ecclesiastes. There is, however, a definite need at the present time for an up-to-date work dealing with river pollution in its various aspects. Since the passing of the River Boards Act, 1948, and the Rivers (Prevention of Pollution) Act, 1951, there has been widespread interest in the condition of our rivers and a demand for purer rivers by fishery interests, water undertakings and, indeed, river users in general. It was to satisfy a need for information on the problems associated with pollution that the author undertook the writing of this book.

The book is divided into 15 chapters each of which covers a particular aspect of river pollution. A short chapter has been devoted to the legal aspects of the subject as applicable to conditions in this country. I have included a chapter on the detection and measurement of pollution which is intended to supplement rather than encroach upon the ground covered by the many practical handbooks on the subject.

I am deeply indebted to Dr J. R. Erichsen Jones, Ph.D., D.Sc., lecturer in zoology, University College of Wales, Aberystwyth, for contributing a chapter on 'Fish and river pollution', and to Mr H. A. Hawkes, M.Sc., A.M.Inst.S.P., biologist to the Birmingham Tame and Rea District Drainage Board for writing a chapter on 'Biological aspects of river pollution'. The book would have been incomplete without these two important chapters. It is a pleasure, also, to express my thanks to Mr J. T. Firth, chief engineer to the Mersey River Board and his staff, particularly Mr R. A. Hargreaves and Miss L. C. James of the gauging department, for the inclusion of Chapter 11. In this chapter some physical characteristics of streams are discussed in relation to pollution. It is customary to use the minimum dry weather flow of a river as a basis for obtaining dilution factors in pollution problems. The dry weather flow, however, can vary seasonally and according to the level of the surrounding water table. We have, therefore, suggested a method of determining what we propose to call the 'standard flow' of a river. This flow (the most frequently occurring dry weather flow) is based upon a statistical evaluation of flow records over a period of at least 10 years and we consider it to be a more appropriate basis for calculating dilution factors.
PREFACE

Notable omissions from this book are the subjects of corrosion and the pollution of tidal waters. Corrosion is already adequately dealt with in several works. The question of the pollution of tidal waters is in a different category since much work remains to be done on this subject which some day might well form the theme of a whole volume.

It is not possible within the limits of a single book to deal exhaustively with the many aspects of river pollution. Each chapter, however, is provided with its own list of references which will enable the reader to study the subject matter in greater detail should he so desire. The total number of references exceeds 1,300 but many thousand would be required for a complete survey of the literature. In this connection, I must express my indebtedness in my search of the literature to the excellent Water Pollution Abstracts published monthly for the Water Pollution Research Laboratory by H.M. Stationery Office, London; and to the 20-year Index (1928-48) for the American Sewage Works Journal published by the former Federation of Sewage Works Associations (now the Federation of Sewage and Industrial Wastes Associations). Much of the information presented in this book is widely scattered throughout the literature and has now been collected together in one volume for the first time.

Although intended more particularly for those directly concerned with anti-pollution work, such as Government departments, river boards, local authorities, water undertakings, manufacturers, and the great nationalized undertakings, the book should also make an appeal to public analysts, consultants, sanitary inspectors, engineers, medical and public health authorities, anglers, and indeed all who value the purity of our rivers and the beauty of our countryside. Although the book is written primarily from the standpoint of British practice, much of the subject matter has application to conditions in other countries.

I am fully conscious that in many instances I have only dealt inadequately with certain topics. To do full justice to a many-sided subject like river pollution would require not one book but many volumes. Consequently, to those critics who complain of certain shortcomings in this book, I would plead, as did Samuel Johnson in the preface to his dictionary 'In this book, when it shall be found that much is omitted, let it not be forgotten that much likewise is performed'.

I am greatly indebted to Mr A. H. Jolliffe, clerk of the Mersey River Board and to many colleagues on the staff of the Board for their invaluable assistance in the preparation of this book. In particular, it gives me great pleasure to thank Mr H. Greenhouse, A.R.San.I., and Mr R. Bolton, A.M.C.T., M.R.San.I., M.Inst.S.P.
(district inspectors), Mr A. McKay, F.R.I.C. (senior assistant chemist), Mr D. Higham, B.Sc., Mr C. J. Carroll and Miss S. M. Turner, B.Sc. (assistant chemists), for reading and criticizing several of the chapters and for assistance in the preparation of some of the diagrams. I should like also to express my appreciation of the valuable critical comments made on several of the chapters by Dr T. Stones, M.Sc., F.R.I.C., manager and chemist to the Salford Corporation Sewage Works. Assistance with the photographs of some of the organisms in Chapter 8 has been given by Mr C. M. G. Keeping, A.R.I.B.A., architect, Birmingham Tame and Rea District Drainage Board, and by Mr G. F. Dixon, Member of the Birmingham Natural History and Philosophical Society, to both of whom I would express my grateful thanks. I am indebted to the divisional controller of the Central Electricity Authority for his kindness in allowing me to publish, in Chapter 5, figures relating to some generating stations in Lancashire. It is a pleasure also to thank the United States Public Health Service for permission to quote their drinking water standards; and Dr B. A. Southgate, C.B.E., director of the Water Pollution Research Laboratory, for his kindness in allowing me to reproduce a table showing the solubility of oxygen in water which is based on the most recent work carried out by that laboratory.

I am very grateful to the Editor of the American Sewage Works Journal (now Sewage and Industrial Wastes) for permission to quote material from that publication; to the Editor of the American Journal Water and Sewage Works for his courtesy in allowing me to reproduce Figure 2, from a paper by Thomas, and other material from that journal; to Dr B. A. Southgate, C.B.E., for allowing me to reproduce a photograph of Beggiaea (Plate V a) from a paper by Mr T. G. Tomlinson, M.Sc., of the Water Pollution Research Laboratory; to Mr T. G. Tomlinson, M.Sc., for permission to reproduce a hitherto unpublished photograph of Carchesium (Plate V c); and to the Controller of H.M. Stationery Office for his kindly allowing me to reproduce a photograph of Leptomitus lacteus (Plate V b); and finally to Mr W. T. Lockett, Editor of the Journal of the Institute of Sewage Purification, not only for his kind permission to quote material from that journal but also for allowing me to reproduce photographs of organisms (Plates I a, I b, I c, II a, VI a, and VI b) from a paper in the Journal by Mr H. A. Hawkes, M.Sc., and Dr S. H. Jenkins.

Any corrections or suggestions for the improvement of this book will be welcomed by the author.

Manchester
July, 1956

L. KLEIN
ABBREVIATIONS

A.P.H.A. American Public Health Association
B.D.H. British Drug Houses
B.O.D. Biochemical Oxygen Demand
D.W.F. Dry Weather Flow. This term is applied to the normal flow of a stream, or of the sewage at a sewage works, during dry weather which extends over the whole catchment or drainage area. There is no general agreement on what constitutes ‘dry weather’.

m.g.d. million gallons per day
M Molar, i.e. a solution containing the molecular weight in grammes of a substance per litre of the solution
N Normal, i.e. a solution containing 1 gramme equivalent of substance, or amount of substance equivalent to 1.008 grammes of hydrogen, per litre of solution
p.p.m. parts per million (i.e., grammes per million millilitres,* or milligrammes per litre)
rev/min revolutions per minute
sp. species (singular)
spp. species (plural)
e the base of natural logarithms ( = 2.71828... )
< less than
> greater than
g/l. grammes per litre
mg/l. milligrammes per litre
mV millivolts
atm atmosphere (pressure) = 14.7 lb./in.²
lb./min.² pounds per square inch
h hours
ft.³/sec cubic feet per second (cusec)
gal./day gallons per day
ft.³ cubic feet
µg microgrammes
ml millilitres
gr grains
µcurie/l. micro-curie per litre

The abbreviations appearing in Chapter References are taken from World List of Scientific Periodicals (Butterworths, London).

* Definition given by Ministry of Housing and Local Government in Circular No. 834, 1954. In British units, it is, for all practical purposes, approximately equal to lb. per million lb. or lb. per 100,000 gal.
CHAPTER I

HISTORICAL INTRODUCTION

Thou shalt have a place also without the camp, whither thou shalt go forth abroad: And thou shalt have a pottle upon thy weapon; and it shall be, when thou wilt ease thyself abroad, thou shalt dig thereby, and shalt turn back and cover that which cometh from thee.

Old Testament. Deut. xxiii. 12-13

Cleanliness is next to Godliness.

CHARLES DICKENS (1812-70)

Great Expectations, ch. 4

The disposal of human wastes and other organic refuse without creating a nuisance has been a problem since time immemorial. One of the foremost of the early sanitarians, Moses, framed a very striking and comprehensive code of health regulations for the ancient Israelites and, as the quotation given above shows, the difficulty in the disposal of human waste products was surmounted by resorting to burial of the wastes in the earth. We now know that this procedure has a sound scientific basis. It involves the breaking down of organic matter by soil bacteria to harmless and indeed useful end-products. In this way, the waste products thus restored to the soil are converted to food for plant life which, in turn, becomes again the food of animal life and man. The method is a reasonably satisfactory one so long as the population is not too large and plenty of land is available. China with her vast areas of land has for centuries practised the method of returning to the soil all vegetable, animal and human wastes and has thus been able to maintain large populations without any marked falling off in soil fertility. The problem, however, becomes more complicated when mankind seeks to live in large cities. Fowler1 points out that in ancient days in India towns and villages were evacuated from time to time by the population and re-established elsewhere so that the impurities of many years could be broken down by natural agencies. Long before even the days of Moses, Zoroastrianism, the religion of the ancient Persians, laid great stress on purity and the health of mind and body, and definitely forbade the discharge of organic refuse or indeed any filth into the rivers. In modern India, on the other hand, the Manchester Guardian (8 July 1953) has reported that a fast unto death was being carried out by a 'Holy Man' in
In order to obstruct the passing of a Bill for the prevention of river pollution!

In a fascinating paper dealing with sewerage in ancient and medieval times, Gray has pointed out that several ancient empires in Assyria and Babylonia possessed sanitary systems which would put to shame those in some of our modern towns. Both the Indus civilization (about 2550 B.C.) and the Aegean civilization (about 3000-1000 B.C.) possessed quite elaborate drainage systems constructed of brick or stone. For example, on the island of Crete, A. Mosso, quoted by Gray, made the following remarkable statement:

One day, after a heavy downpour of rain, I was interested to find that all the drains acted perfectly, and I saw water flow from sewers through which a man could walk upright. I doubt if there is any other instance of a drainage system acting after 4000 years.

The sewers of Rome are, of course, quite famous but they were intended to be used for the removal of rain water and underground water and not as sewers. Indeed, the filth of Rome went into the Tiber, and Reynolds goes so far as to say that the neglect of sanitation in the declining days of Rome was the cause of the general increase of malaria, the decline in the health of the people, and the depopulation of the cities.

During the Middle Ages, when habits of cleanliness were at a low ebb, the streets in the cities of Europe were foul with excrement and filth, and the stench must have been well nigh intolerable at times. Gray, referring to the perils of the passer-by in the streets of those days, states that Parisians freely emptied chamber-pots from their windows and only the nimble and lucky escaped being drenched! It is even recorded that Shakespeare's father had to appear before the Burgesses of Stratford on Avon and was severely reprimanded for failing to remove dung from the front of his house. Small wonder, then, that the aristocrats of the day when walking abroad often held a clove-studded orange to their nostrils in order to make the atmosphere more tolerable.

Undoubtedly many of the plagues and epidemics that raged from time to time in those days had their origin in the insanitary habits of the people. Unfortunately, epidemics resulting from primitive or non-existent sanitation were, as Kempster has pointed out, popularly regarded as an Act of God or the Devil. This is very different from the twentieth-century attitude and in these times, as the Archbishop of York suggested at the Royal Sanitary Institute Congress held in York in 1912, it would be regarded as akin to blasphemy to say that 'an outbreak of disease is God's will.
being done, when patently it is man's duty which is being left undone'.

The introduction about 1810 of the modern water-carriage system of sewage disposal in the towns and cities of England merely transferred the filth from the streets to the rivers. The problem was intensified in Britain by the coming of the Industrial Revolution and the establishment of factories on the banks of rivers where water was freely available for power and for manufacturing processes. This meant that large quantities of liquid and solid trade wastes, as well as crude sewage, found their way to the rivers. Many of the rivers were little better than open and stinking cesspools; fish which were formerly abundant disappeared and even water supplies were in danger. Thus, by about the middle of the nineteenth century pollution of streams had become a very serious menace to public health, particularly in such densely populated areas as Lancashire, Yorkshire, the Midlands and London. For example, in London, the result of discharging untreated sewage from a large and increasing population into the River Thames soon became manifest. Dr. William Budd, quoted by Gray², describes very tellingly the noxious odours proceeding from this river during the years 1858-9:

'For the first time in the history of man, the sewage of nearly 3,000,000 people had been brought to seethe and ferment under a burning sun, in one vast open cloaca lying in their midst. The result we all know. Stench so foul, we may well believe, had never before ascended to pollute this lower air. . . . For many weeks, the atmosphere of Parliamentary Committee rooms was only rendered barely tolerable by the suspension before every window of blinds saturated with chloride of lime, and by the lavish use of this and other disinfectants. More than once, in spite of similar precautions, the Law Courts were suddenly broken up by an insupportable invasion of the noxious vapour. . . . Day after day, week after week, The Times teemed with letters, filled with complaint, prophetic of calamity, or suggesting remedies.'

And, indeed, calamity did arise in London in the form of two great epidemics of cholera in 1866 and 1872.

Conditions in Lancashire were at least as bad. As far back as 1721 fishing was still an important industry on the River Mersey and the River Irwell. In fact, the local fishermen of the day were violently opposed to the scheme put forward to make the rivers navigable from Liverpool to Manchester. Up to about 1780, the use of these rivers for drinking water and for the washing of clothes was still common practice. During the late eighteenth century and
early nineteenth century, however, there was a tremendous growth of industry and population. The great cotton industry of Lancashire, as well as numerous tanneries, paper mills, chemical works and gas works, produced extremely polluting wastes which were discharged directly to the rivers together with crude sewage from an ever increasing population. There is little cause for wonder, then, that by the early nineteenth century all fish life and other aquatic life, animal and vegetable, had virtually disappeared. Turpin has reported that, at one time, the scum in parts of the River Irwell was so thick and solid that birds walked on it without sinking. It may have been some such condition as this that inspired the following humorous lines which, according to Johnson, were found on a board room table after a meeting of the Mersey and Irwell Joint Committee about the year 1901:

'If with a stick you stir well
The poor old River Irwell,
Very sick of the amusement
You will very soon become;
For foetid bubbles rise and burst
But that is really not the worst
For little birds can hop about
Dry-footed on the scum.'

An American counterpart is reported by Fuller and McClintock who state that at one time one of the branches of the Chicago river (appropriately called 'Bubbly Creek') became covered with such a thick scum that people were able to walk upon it quite safely.

At last, the Government decided that something ought to be done to combat the steadily increasing pollution of the country’s rivers and two Royal Commissions on Rivers Pollution were appointed to study and report on the problem, one in 1865 and the second in 1868. The 1st report of the 1868 commission stated that ‘of the many polluting liquids which now poison the rivers, there is not one which cannot be either kept out of the streams altogether, or so far purified before admission as to deprive it of its noxious character’. The 3rd report of the 1868 commission contains very convincing evidence of the shocking state of the Yorkshire River Calder in the shape of a memorandum from an angry manufacturer written not in ink but with ‘river water taken this day from the point of junction between the River Calder and the town sewer’. The writer added: ‘Could the odour only accompany this sheet, it would add much to the interest of this memorandum!’

The evils of river pollution so convincingly brought home by the reports of these two commissions were now beginning to awaken the public conscience and to stir governing circles into legislative
action. The result was the passing by the Disraeli Government of the Public Health Act, 1875, rightly regarded as one of the foremost sanitary measures of our times. This Act clearly recognized for the first time that care of public health was a national responsibility and established a system of local health administration setting down amongst other things the duties of local authorities with regard to the disposal and treatment of sewage. Sewage was to be 'free from all excrementitious or other foul or noxious matter such as would affect or deteriorate the purity and quality of the water in any stream into which it is discharged', but unfortunately the technique of sewage purification had not yet advanced sufficiently to make this Utopian Ideal practicable. The Act of 1875 was followed in the succeeding year by another famous enactment which for the first time attempted to control the pollution of rivers by sewage and industrial wastes, namely the Rivers Pollution Prevention Act, 1876, which applied not only to England and Wales but also, with modifications, to Scotland and Ireland. This Act formed, until as recently as 1951, the basis of all legal action connected with pollution of rivers (see Chapter 2).

Part I of the 1876 Act made it an offence to put solid matter into a stream but it was necessary to prove that either pollution or interference with flow was caused.

Part II prohibited the discharge of solid or liquid sewage matter into a river and it was no defence to argue that the river had already been polluted by sewage upstream.

Part III of the Act dealt with manufacturing and mining pollution and Section 4 prohibited the discharge of any poisonous, noxious or polluting liquid from any factory or manufacturing process. Unfortunately, there was an amending clause in Section 6 according to which the Local Government Board 'shall not give their consent to proceedings by the Sanitary Authority of any district which is the seat of any manufacturing industry unless they are satisfied, after due inquiry, that means for rendering harmless the poisonous, noxious or polluting liquids proceeding from the processes of such manufactures are reasonably practicable and available under all the circumstances of the case, and that no material injury will be inflicted by such proceedings on the interests of such industry ...'. This amendment virtually nullified the important prohibition contained in Section 4, though no doubt it was considered necessary in order to avoid the closing down of those industries which could not comply with the law.

Part IV of the Act dealt with the administration of the law. The most interesting section, anticipating in many ways the 1937 Drainage of Trade Premises Act (see Chapter 2), enabled manufacturers to discharge their trade wastes to a local authority's
sewers subject to the conditions that the wastes must not affect adversely the sewers and that the sewerage system must be large enough to take the wastes.

Although the 1876 Act was in many ways a comprehensive and clearly drafted measure, it was to some extent in advance of its time. The administration of the law was in the hands of the sanitary authorities who were nearly all themselves gross polluters so it is not difficult to see why the Act was for all practical purposes only of limited value. Moreover, it was found in practice that it was comparatively easy for a manufacturer to evade the Law especially by making use of the amending clause in Section 6 of Part III referred to previously. Parliament had no doubt good reasons for the lenience it had hitherto shown towards manufacturers. Perhaps an explanation of this attitude is to be found in a passage quoted by Wilson and Calvert from an article in the Nineteenth Century in 1903 by the Right Hon. C. G. Milnes Gaskell:

'The manufacturers were too powerful a body to be compelled to do their duty. "Parliament"., I once said to Mr. Gladstone during the last year of his life, "has been very lenient to the manufacturers." "Say far too cowardly", replied Mr. Gladstone.'

The duty of enforcing the 1876 Act was originally entrusted to the sanitary authorities (Town Councils, Urban and Rural District Councils) but the Local Government Act of 1888 gave similar powers to the County Councils. Later, river authorities were set up in some of the chief industrial areas to administer the 1876 Act, e.g.

The Mersey and Irwell Joint Committee, 1891.
The Ribble Joint Committee, 1891.
The West Riding of Yorkshire Rivers Board, 1893.
The River Dee Joint Committee, 1932.

Two other boards, namely, The Thames Conservancy Board, first incorporated in 1857 and the Lee Conservancy Board (an ancient board re-constituted in 1868) were originally intended mainly to control navigation only but were given anti-pollution powers which in many respects were wider than those conferred by the 1876 Act. These six river authorities, who did much valuable pioneering work, were, together with some fishery boards, the only means of enforcing the law until comparatively recent times (see Chapter 2) when under the River Boards Act of 1948 river boards were set up covering all the watersheds in England and Wales.

Much progress was made in England towards the end of the nineteenth century in the biological purification of sewage on filters,
which proved to be a great improvement on the existing land treatment method. A Royal Commission on Sewage Disposal was appointed in 1898 to report on methods for the treatment and disposal of sewage and trade wastes. This historic body sat for seventeen years and carried out many important original investigations. It is impossible to praise too highly the painstaking work of this commission whose labours resulted in the publication of nine voluminous reports covering nearly 8,000 pages.

The 1st Report (1901) was of an interim nature and dealt with land treatment of sewage and with various artificial processes for the treatment of sewage (e.g. septic tanks, contact beds, continuous filters and chemical methods).

In the 2nd Report (1902) the evidence of experts on the bacteriology of sewage was given.

The 3rd Report (1903) gave the commission’s views on the treatment of trade effluents and on the relations between local authorities and manufacturers regarding the disposal of trade wastes. One of their recommendations is of particular interest today inasmuch as it anticipated the Public Health (Drainage of Trade Premises) Act of 1937:

'We are, therefore, of opinion that the law should be altered so as to make it the duty of the Local Authority to provide such sewers as are necessary to carry trade effluents as well as domestic sewage, and that the manufacturer should be given the right, subject to the observance of certain safeguards, to discharge trade effluents into the sewers of the Local Authority if he wishes to do so... the Local Authority should frame regulations which should be subject to confirmation by a Central Authority... these regulations could provide definite standards for the different manufacturers as regards preliminary treatment...'

The 4th Report (1904) considered the pollution of tidal waters with special reference to the contamination of shell fish.

The 5th Report (1906) was in effect a comprehensive treatise on methods available for the purification and disposal of sewage. The important conclusion was reached that ‘it is practicable to purify the sewage of towns to any degree required, either by land treatment or by artificial filters’.

In the 6th Report (1909), the question of the disposal and purification of wastes from distilleries was considered.

The 7th Report (1911) dealt with nuisances due to excessive growth of green sea weeds in estuaries polluted by sewage.

The 8th Report (1912) dealt with the contamination of shell fish and with the purification of sewage and trade effluents discharging...
to streams. The oft-quoted 'Royal Commission' standards for sewage effluents based on B.O.D. and suspended solids are to be found here, and there is also a classification of rivers based on their B.O.D. and biological condition.

The 9th Report (1915) is also of great interest as it goes into the question of standards for trade wastes which for some reason cannot be taken into the public sewers and must therefore be discharged to a river.

There is also a Final Report, published in 1915, summarizing the recommendations of the earlier reports. Such was the thoroughness and care with which the Royal Commission carried out its stupendous task that many of the conclusions and results given in the reports are still quoted today.

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2 Gray, H. F., 'Sewerage in ancient and medieval times', *Sewage Wks J.*, 12 (1940) 939-46
8 Reports of Royal Commissions on Rivers Pollution: 1st Commission, 1865-68, 3 Reports; 2nd Commission, 1868-74, 6 Reports. H.M.S.O., London
9 Public Health Act, 1875. H.M.S.O., London
10 Rivers Pollution Prevention Act, 1876. H.M.S.O., London
CHAPTER 2

LEGAL ASPECTS OF RIVER POLLUTION

It is a very easy thing to devise good laws; the difficulty is to make them effective.

Viscount Bolingbroke (1678-1751)

In 1937 the Minister of Health set up the Central Advisory Water Committee under the chairmanship of Field Marshal The Lord Milne for the purpose of advising on questions relating to the conservation and supply of water and the co-ordination of water interests. The 3rd Report of that committee was issued in August 1943, and recommended the formation of new river boards which would replace certain of the existing bodies and be vested with their powers and duties. The committee considered and rejected the idea of legislation to compel the formation of statutory committees solely for the purpose of dealing with river pollution and thought that advisory committees would hardly be able to co-ordinate the many questions which would arise in connection with river control.

No doubt as a result of this report Parliament, in 1948, passed the River Boards Act, described as an Act to provide for establishing river boards and for conferring on, or transferring to, such boards functions relating to land drainage, fisheries and river pollution. Such a board is a single authority having under its control a river system or group of river systems whose boundary, like the catchment boards it replaced, follows geographical features and not local government divisions. The whole of England and Wales is thus covered by 34 authorities, a figure which includes the River Lee Catchment Area and the River Thames Conservancy, to which special legal provisions apply. The functions of these two bodies, however, do include the enforcement of the Rivers (Prevention of Pollution) Act, 1951, to which extensive reference is made later.

Each river board is established by an order made by the Ministers of Housing and Local Government and of Agriculture, Fisheries and Food, and that order lays down the number of members making up a board, in the proportions laid down by the Act—not more than forty except in one or two cases when the National Coal Board have a representative. One of these members is appointed by the

* Does not apply to Scotland or Northern Ireland.
† Formerly the Ministry of Agriculture and Fisheries.
Ministers; a number represent the County Councils and County Borough Councils in the area; and a number, appointed by the Minister of Agriculture, Fisheries and Food, represent lowland drainage areas and fishery interests.

An example of a board of the maximum size is the Mersey River Board, whose area is largely industrial and urban (with a population of about four and a quarter millions) and whose rivers have few fish but are bedevilled with industrial wastes of almost every type. The board consists of the Ministers' representative, 17 members for County Boroughs, 9 for County Councils and 13 to represent lowland drainage areas and fishery interests. River boards do not have among their members any representatives of industrial users of rivers, either as consumers of the water or carriers of their waste as, for example, did the Lancashire Rivers Board, a pollution authority which came to an end with the establishment of river boards and which was required to have a representative of the Federation of British Industries, but river boards may co-opt on their committees up to one-third of their number.

To these river boards the pollution powers of local authorities and the powers and duties of the few special pollution bodies were transferred, and every river board then had power to enforce the provisions of the Rivers Pollution Prevention Act, 1876, in relation to any stream in the board's area.

The Central Advisory Water Committee, whose activities contributed so largely to the setting up of river boards, set up, in 1946, a Rivers Pollution Prevention Sub-Committee to investigate measures for strengthening the law regarding the prevention of pollution of rivers and streams. In that sub-committee's view the need for the improvement of the condition of rivers and streams in many parts of the country could hardly be exaggerated, and they proceeded to suggest such amendments of the law as they considered necessary to enable the appropriate authority to prevent and check pollution whilst having regard to the interests of all parties concerned. Their principal recommendations, or at any rate most of them, were embodied in a Bill which was speedily passed through Parliament in the 1951 session, and came on to the statute book as the Rivers (Prevention of Pollution) Act, 1951.

The principal object of the Act, which replaced the Rivers Pollution Prevention Act, 1876, and local Acts like those of the

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* It is necessary to avoid confusion between the old Lancashire Rivers Board and the new Lancashire River Board formed as a result of the River Boards Act. The old board, an anti-pollution authority covering roughly the whole of Lancashire, was established by the Lancashire County Council (Rivers Board and General Powers) Act, 1936. The new Lancashire River Board is an all-purpose authority covering mainly North Lancashire, the highly industrialized southern part of Lancashire being covered by the Mersey River Board.
Lancashire County Council and the West Riding of Yorkshire, is described as making new provision for maintaining or restoring the wholesomeness of the rivers and other inland or coastal waters of England and Wales. It seeks to achieve that aim by prohibiting the use of any stream for the disposal of polluting matter or refuse, and the offence of so doing (unlike under the Rivers Pollution Prevention Act, 1876, offences against which were triable before a county court judge) can be dealt with by a local bench of magistrates. There is an alternative procedure, this time before a county court judge, for an order preventing the use of a stream for the disposal of poisonous, noxious or polluting matter and for making good defaults.

The Rivers Pollution Prevention Sub-Committee contemplated that it would be practicable to lay down certain standards for effluents and the Act provides for by-laws containing those standards and prohibiting the putting of litter into streams, or washing things of any class or description therein. The Act does not extend to estuaries and coastal waters, but is capable of being so extended by an order of the Minister of Housing and Local Government. Section 7 of the Act is of particular interest since it makes a new outlet or a new discharge illegal unless the board have first consented thereto and, subject to appeal to the Minister, such a consent can be subject to conditions within the limits laid down in the section. In general it is not open to the public to take any proceedings for a contravention of the Act; such proceedings can only be instituted by the Attorney-General or by a river board, and a prosecution under the two sections which deal with the prohibition of the use of a stream for the disposal of polluting matter will require, for a period of seven years since the passing of the Act, the consent of the Minister, although such consent is not necessary in connection with an offence against by-laws prescribing standards, etc.

As will be noted in the previous chapter, the consent of the Minister to proceedings in connection with trade wastes is nothing new, but it is new in connection with the taking of proceedings against a local authority for a bad sewage effluent. This was inserted by the Ministry in the draft Bill despite the views of the Rivers Pollution Prevention Sub-Committee of the Central Advisory Water Committee. Although such a suggestion was made to the committee it did not think 'there was any ground for making such an addition to the law nor was there any request for such protection from Local Authorities who were chiefly concerned'.

The first offence, and the main one, is in Section 2 and is that of putting into a stream any poisonous, noxious or polluting matter, to which it is a defence to say that a trade effluent or effluent from a local authority's sewage works cannot reasonably be otherwise disposed of except into a stream and all reasonable steps have been
taken to prevent the effluent being unnecessarily poisonous, noxious or polluting. Of these words the learned editors of *Lumley's Public Health* write, 'these three words must have separate meanings; "poisonous" implies destruction of life, human or animal; "noxious" is lower in degree, and signifies some injury, but not of necessity immediately dangerous to life; "polluting" will include both the other qualities and also what is foul and offensive to the senses.'

It has, however, long been laid down by the courts that what matters is what goes into the stream, not the condition of the stream into which it goes, and the offence is to add something which would pollute the stream if its water were pure. The offence carries the substantial penalty of up to two hundred pounds if on indictment, or fifty pounds summarily and, when the offence is repeated or continued, imprisonment may be imposed. As the approval of the Ministry of Housing and Local Government is required to such proceedings, unless the river is one for which by-laws are in force fixing standards prescribing what is to be treated as poisonous, noxious or polluting, the Ministry has published the information which it must have before considering any application for consent —information which seems to go somewhat farther than would be necessary solely to consider whether the best practicable means are being used to render the polluting liquid harmless.

So long as the power of withholding consent to a prosecution rests with the Minister it is unlikely that any legal guidance will be given by the courts on the factors to be considered in determining what steps are to be regarded as 'reasonably practicable' and what is meant by 'unnecessarily' poisonous, noxious or polluting. It would seem from the information the Ministry requires that the state of the river into which the effluent goes is to be considered in determining whether a waste is unnecessarily polluting.

In Section 3 is another method of dealing with a contravention of the law prohibiting the use of a stream for the disposal of polluting matter (but not a penal one and applicable to a breach which is occurring, new or anticipated), namely, to obtain an order of a county court judge prohibiting the use of (1) a stream for the disposal of any matter, (2) land for the storage of any matter, or (3) permitting it only on terms designed to remove the grounds of complaint. Yet another offence against the Act, if done without the consent of the board, is to clean the channel or bed of a stream from a deposit accumulated by reason of any dam, weir or sluice holding back the water so that the deposit is carried away in suspension in the water of the stream, or by wilful default allow any substantial amount of vegetation cut or uprooted in the stream, or so near that it falls in, to remain in the stream.
Section 5 enables by-laws to be made prescribing standards for the purpose of determining when matter is to be treated as poisonous, noxious or polluting and prohibiting washing or cleansing in a stream of things of any class or description or putting any sort of litter into a stream. The by-laws may fix standards of temperature and, it should be noted, of discoloration and, if complied with, prevent proceedings under the Salmon and Freshwater Fisheries Act, 1923 (to which later reference is made) for causing water to be poisonous to fish or their food. No Ministry consent is required to proceedings for a breach of by-laws.

So far the provisions of the Act, in its application to rivers where no by-laws are in force, aim at making existing discharges as good as is reasonably possible, and, in the words of the Act, not unnecessarily polluting. New discharges are in a different position. Here the river board may lay down conditions as to the nature and composition, temperature, volume or rate of discharge, it being an offence to make a new discharge without the consent of the board. Similarly, a new outlet normally requires the consent of the board and conditions may be imposed as to the point of discharge and construction which must provide facilities for taking samples of the effluent.

The last word as to giving or withholding consent and as to the reasonableness of conditions rests with the Minister, whose permission is not, however, required to proceedings for failing to get consent or observe conditions. A 'new discharge' need not be new in the literal meaning of the word, and the protection a pre-Act discharge enjoys, or one to which conditions have been applied, is lost if there is a substantial change in the nature or composition, temperature, volume, or rate of discharge, or if there is a period of over a year when the discharge is not made. Once consent is given it cannot be withdrawn, but a river board is under a statutory obligation periodically to review conditions and may make reasonable variations.

In many urban districts of small rateable value the sewage works are out of date and the resources of the council, even with grants from County or State funds, unequal to the burden of reconstruction. Often such areas have large industries, the trade wastes from which are too strong or great in volume to be treated by admixture with sewage in the local treatment works. Where such local government areas adjoin another with a sewage works of ample capacity an obvious solution is to join the smaller to the greater, but local pride and fear of amalgamation often prove an obstacle to probable improvement of a stream. In such a case the Minister can either set up a joint board for sewage disposal, make an order requiring the joining up of sewers, or the discharge of the sewage, from one authority to the sewage works of another. So
delicate, however, is this subject that an objection to the Minister's order by a local authority affected becomes a matter for special Parliamentary procedure, whereby objections by the parties are considered by a parliamentary committee hearing evidence and arguments of counsel, and Parliament itself can deal with any objection of principle.

This Act does not apply to Northern Ireland and consequently the Rivers Pollution Prevention Act, 1876\(^{11}\), remains in force, as affected by Section 80 of the Fisheries (Ireland) Act, 1842\(^{12}\), and the Fisheries (Flax Water) Act (N. Ireland), 1947\(^{13}\). Scotland has its own Act\(^{14}\), passed in 1951, and the pollution authority follows a rather different pattern from that in England and Wales, the main difference being that provision was made in the Act for the establishment of 'River Purification Boards' to deal only with pollution prevention and not with fisheries and land drainage. Other differences between the Scottish Act of 1951 and English legislation are discussed in papers by Lover\(^{15}\) and James\(^{16}\). In the Republic of Ireland there is no law specifically designed to ensure the purity of rivers and pollution is linked up with fish by the Fisheries (Statute Law Revision) Act, 1949\(^{17}\), and the Fisheries (Amendment) Act, 1953\(^{18}\). These are enforced by 17 Boards of Fishery Conservators which deal with all the waters of the State.

Other legal provisions affecting rivers can be found in the Public Health Act, 1936\(^{19}\), the Public Health (Drainage of Trade Premises) Act, 1937\(^{20}\), and the Gas Act, 1948\(^{21}\).

The 1936 Act prevents a local authority from putting foul water into a stream before it has been treated so as not to harm the quality of the stream, so that if a discharge into a foul stream does not make it noticeably fouler no offence is committed.

The Public Health (Drainage of Trade Premises) Act, 1937\(^{22}\), gives industry a right to discharge trade effluents into public sewers.\(^*\) This right is subject to the power of the local authority to lay down conditions as to the nature and composition of the effluent, its volume and maximum rate of discharge, and to the power of the Minister to settle disputes. A waste which was being discharged prior to 1937 does enjoy a prescriptive right provided that it remains in all respects substantially unchanged, but if additional buildings are provided from which waste comes, although the volume is not increased, then the exemption is lost\(^{23}\). The Act contemplates that local authorities will make by-laws regulating the admission of trade wastes to the sewers and controlling such matters as volume, temperature, the exclusion of injurious or obstructive matters, the

\* This Act does not extend to Scotland, Northern Ireland, or to the County of London. The London County Council (General Powers) Act, 1953, deals with the discharge of trade effluents to the L.C.C. sewers.
payments to be made and the provisions for sampling, but no local authority has made such by-laws, nor apparently has the Minister exercised his power to make by-laws in case of default, although model by-laws were issued in 1938.

The gas industry is not in so good a position. It is an offence under the Gas Act, 1948, to put gas liquor into a stream, punishable with a fine of two hundred pounds, and the condition of the stream or the difficulty of treating or disposing of the liquor are not factors to be considered.

Certain rights exist at common law which affect the pollution of rivers. These relate or attach to the land through which a stream flows. The right to a flow of pure water is a natural right of property, and a riparian owner on a natural stream having a right to that stream in a natural state has a right of action if the water is polluted, even though in fact he sustains no actual damage. It makes no difference to his rights against one polluter that the river is also polluted from other sources. It is, however, possible to acquire a right to pollute by maintaining a noticeable amount of pollution continuously for twenty years. A careful review of the rights of a riparian owner in these circumstances and remedies open to him will be found in the judgment in the case Pride of Derby and Derbyshire Angling Association Ltd. and others v. British Celalene Ltd., Derby Corporation and the British Electricity Authority. This case also dealt with the peculiar position of two of the polluters who were respectively a local authority, exercising statutory functions, and an electricity authority, and the views of the learned judge, who granted injunctions against all three defendants, were upheld the following year by the Court of Appeal.

At one time fishery boards could take proceedings for pollution in the same way as a sanitary authority could under the Rivers Pollution Prevention Act, 1876, but fishery boards became merged with river boards as a result of the River Boards Act, 1948. A river board can still take the same proceedings as a fishery board could, under Section 8 of the Salmon and Freshwater Fisheries Act, 1923, against anyone who pollutes waters containing fish to such an extent as to be poisonous or injurious to fish or to spawning grounds, spawn or the food of fish, but, for the purposes of that enactment, matter entering a stream is not to be regarded as poisonous or injurious if it complies with a standard prescribed by by-laws.

REFERENCES

ASPECTS OF RIVER POLLUTION


9. *Fisheries (Scotland) Act*, 1923. Sect. 80


ADDITIONAL REFERENCES


WHAT IS RIVER POLLUTION?

It is not easy to give a precise definition of 'pollution' or of the word 'polluting'. The various Acts dealing with river pollution, already discussed in the preceding chapter, constantly make reference to the word 'polluting', but nowhere does this word or the noun 'pollution' receive precise elucidation. In the 1876 Act, the word 'pollutio' is left undefined, but it is stated that it shall not include 'innocuous discoloration'. Most people have fairly definite views as to what constitutes pollution in a stream. If a river is turbid, or coloured, or contains visible suspended or floating matter, or has an objectionable smell, then it is rightly regarded by the average person as 'polluted'.

The word 'pollution' is derived from the Latin word *pollutus*, past participle of the verb *polluere*: to soil, to defile. The *Oxford English Dictionary* defines 'pollute' and 'pollution' as follows:

- To pollute: to make physically impure, foul, or filthy; to dirty, stain, taint, befoul.
- Pollution: the act of polluting or condition of being polluted; uncleanliness or impurity caused by contamination.

Thus, it is apparent that pollution, so far as rivers are concerned, can have two meanings, namely (1) the act of polluting or fouling the stream, and (2) the actual impurity or contamination introduced into the watercourse.
Coulson and Forbes', in their monumental work *The Law of Waters*, give a definition of 'pollution' having special application in common law: 'the addition of something to water which changes its natural qualities so that the riparian proprietor does not get the natural water of the stream transmitted to him'. They then give three typical examples of pollution which illustrate this definition and which have formed the basis of successful legal action, viz.

(i) addition of hard water to soft water
(ii) the raising of the temperature of water, and
(iii) the addition of something which on meeting some other substance already in the water, each in themselves harmless, causes pollution.

Obviously, the term 'pollution' as defined in common law has its widest and broadest significance, but it certainly has a somewhat narrower meaning in the various statutes dealing with pollution.

From the scientific standpoint, it is perhaps easier to regard pollution as the actual impurity introduced into the stream rather than the act of introducing such impurity, and to define pollution as 'anything causing or inducing objectionable conditions in any watercourse and affecting adversely any use or uses to which the water thereof may be put'.

Since pollution markedly affects the flora and fauna of a stream and can alter the number of individuals as well as the number of species, it can also be defined in relation to its effects on plant and animal life in the river (see Chapter 8).

It is of interest to note that in the State of California, U.S.A., the new control laws since 1950 make a distinction between 'contamination' and 'pollution'. 'Contamination' is regarded as 'the impairment of water quality by sewage or industrial waste causing an actual hazard to public health or an equivalent effect, whether or not waters of the State are affected'; power to take immediate action is given in this case as a direct menace to public health is involved. On the other hand, 'pollution' involves the introduction of anything which 'adversely and unreasonably impairs the beneficial use of water even though actual health hazard is not involved'; slower more deliberate methods are used here. The reason for separating the two categories evidently derives from the much greater need for speedy action in cases where a potential danger to public health is involved.

It may happen that substances not normally regarded as polluting can, under special circumstances, become so. Nitrates, which are present in well-purified sewage effluents and so find their way to streams, provide an interesting example. Firstly, under certain circumstances, nitrates can stimulate the growth of algae to such
an extent as to cause the water to become objectionable (see page 83). Secondly, it has been shown by many workers\textsuperscript{1,4,5} that young infants (usually less than six months old) receiving artificial feeds of milk diluted with water containing more than about 10–20 p.p.m. of nitrate (expressed as N), may develop a disease called ‘methaemoglobinemia’, whereas no cases are observed amongst breast-fed infants. This disease, which is often fatal, is characterized by the development of a greyish-blue or brownish-blue cyanosis which eventually covers the whole body and is caused by the partial conversion of haemoglobin to methaemoglobin by nitrates formed by the reduction of nitrates. The work of Cornblath and Hartman\textsuperscript{6} has shown that in this way only very young babies having gastric juice with a pH value greater than 4·0 (i.e. no free hydrochloric acid present) and nitrate-reducing bacteria in the upper gastro-intestinal tract develop methaemoglobinemia; apparently these bacteria only flourish on account of the lack of mineral acidity in the gastric juice, which explains why older children with adequate gastric acidity are not subject to the disease. Since it is difficult to remove nitrates from water, the only cure is to change the water to one of low nitrate content.

**THE DIFFERENT KINDS OF POLLUTION**

Pollution may be solid or liquid, and if liquid, may contain dissolved material or suspended matter as well as dissolved gases of a polluting character.

Solid pollution may consist of any kind of solid material, such as sand, gravel, soil, ashes, cinders, clinkers; sweepings from any factory, mine, quarry, or house; any sludge or solid sewage matter; any vegetable or other garbage; offal or parts of the carcase of any animal; rubber, wood, paraffin wax, gelatine, straw, paper or paper pulp, and even bread and butter!

The commonest form of pollution causing the most trouble to river authorities, however, is liquid (which includes solids in suspension), and this is generally caused by the discharge of sewage and industrial wastes into rivers.) A classification of the kinds of pollution found in sewage and trade wastes is given in Table I.

(Chemical pollution, due to the presence of organic or inorganic substances, is, in general, the commonest type of pollution and the most intractable.) Oil in a stream, though perhaps strictly a physical form of pollution, will be discussed for convenience along with the chemical kinds of pollution (pages 23–5). It must be noted, too, that with the exception of temperature the physical and physiological manifestations of pollution are, strictly speaking, secondary phenomena arising from the presence of small quantities, often the
merest traces, of chemical substances. Thus, foam can originate from the discharge of quite small amounts of synthetic detergents to a stream; radioactivity is caused by the breakdown of minute quantities of certain unstable elements and their compounds; turbidity can be due to the presence of small amounts of clay or other substances in the colloidal state; and finally odour and taste can be acquired by waters having the merest traces of certain odour-producing and taste-producing chemical compounds. The classification given in Table 1 is, however, convenient, even if not strictly accurate, from the scientific viewpoint.

<table>
<thead>
<tr>
<th>A. Chemical</th>
<th>B. Physical</th>
<th>C. Physiological</th>
<th>D. Biological</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic (carbon compounds)</td>
<td>Colour</td>
<td>Taste</td>
<td>Bacteria (pathogenic)</td>
</tr>
<tr>
<td>Inorganic (mineral compounds)</td>
<td>Turbidity</td>
<td>Odour</td>
<td>Viruses</td>
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<tr>
<td></td>
<td>Temperature</td>
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<td>Animals</td>
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<td></td>
<td>Suspended matter</td>
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<td>Foam</td>
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<td></td>
<td>Radioactivity</td>
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A detailed discussion of the various kinds of pollution now follows.

**CHEMICAL TYPES OF POLLUTION**

**ORGANIC POLLUTION**

This extremely common form of pollution is due to the presence of proteins, fats, carbohydrates and other organic substances and materials found in sewage and trade wastes. The nature, composition, properties and occurrence of the more important types of organic compound, in so far as these have a bearing on the pollution problem, will now be discussed.

Proteins are nitrogenous organic substances of high molecular weight found in the animal and vegetable kingdom and consisting wholly or partly of very large numbers of amino acids united by their carboxyl- and amino-groups. Examples are egg albumin, gelatine (found in bones and other animal tissues), keratin (present in wood), fibroin (present in natural silk), casein (found in milk), and glutenin (present in wheat). Different proteins vary amongst themselves in composition. They all contain carbon, hydrogen, oxygen and nitrogen; most contain sulphur and some contain phosphorus as well. A typical protein has the following approximate composition: C, 52 per cent; H, 7 per cent; O, 22 per cent; N, 16 per cent.
S, 0·4-2 per cent; P, 0·2 per cent. (Under the influence of bacteria and other micro-organisms, proteins readily undergo putrefaction giving chiefly amino acids, fatty and aromatic acids, and numerous organic bases (e.g. lower aliphatic amines, putrescine, cadaverine, indolethylamine, indole, skatole) as well as sulphuretted hydrogen (H₂S), and organic sulphur and phosphorus compounds. Many of these decomposition products have very objectionable odours.) Excreta and fresh sewage are said to owe their unpleasant smell largely to the presence of small amounts of indole and its methyl derivative, skatole:

According to Rudolf and Chamberlin, results at the Madison–Chatham sewage works showed that indole was present to the extent of 0·25 parts per 1,000 million in the raw sewage and skatole to the extent of 0·19 parts per 1,000 million, but only traces of these substances were found in the treated effluent from the activated sludge plant.

Among the trade wastes containing proteins are food processing and canning wastes, gelatine and size manufacturing wastes, slaughterhouse wastes, dairy wastes and tannery wastes. The grossly polluting character of all these wastes is due in no small degree to their protein content.

Fats, which include animal and vegetable oils, are esters of the trihydric alcohol glycerol (CH₂OH·CHOH·CH₂OH) with the higher fatty acids (e.g. palmitic, stearic and oleic acids). They have the general constitution:

\[
\begin{align*}
\text{CH₂OR'} & \\
\text{CH₃OR''} & \quad (R', R'' \text{ and } R''' \text{ are identical or different fatty acid residues})
\end{align*}
\]

Although insoluble in water, fats dissolve in such organic solvents as petroleum, chloroform, and ether.

When boiled with alkali, or subjected to the action of micro-organisms, fats break down to glycerol and fatty acids. The higher fatty acids so formed can undergo further decomposition to the
22 ASPECTS OF RIVER POLLUTION

lower fatty acids, many of which (butyric acid, valeric acid, etc.)
have unpleasant rancid odours.

Fats occur in sewage and in such industrial wastes as wool
scouring wastes, edible oil and fat refining wastes, wastes from soap
manufacture, and laundry wastes.

Soaps are strictly any metallic salts of the higher fatty acids, or
of resin acids, but in common parlance the term is restricted to the
water-soluble sodium and potassium salts. The sodium salts
('hard' soaps) and potassium salts ('soft' soaps) are prepared by the
saponification of fats with boiling solutions of caustic soda and
caucistic potash respectively. Thus, the fat palmitin is converted
by caustic soda to the soap, sodium palmitate, and glycerol according
to the equation:

\[
\text{Palmitin} \rightarrow \text{Sodium palmitate} + \text{Glycerol}
\]

\[
\text{CH}_2\text{O}\cdot\text{CO}\cdot\text{C}_8\text{H}_{17} + \text{CH}_2\text{OH} \rightarrow \text{Na}^+\text{C}_8\text{H}_{17}\text{COO}^- + \text{CH}_2\text{OH}
\]

In addition to the water-soluble sodium and potassium soaps,
there are also the water-insoluble soaps of such metals as calcium,
iron, aluminium, manganese, lead, and zinc. Many of these
metallic soaps are used industrially, for instance aluminium,
zinc, and lead soaps in certain lubricants and greases, and man­
ganese, lead and cobalt soaps in the manufacture of paints and
varnishes.

JEPSON and KLEIN have shown that certain metallic soaps (e.g.
calcium oleate, ferric stearate, and a ferric soap prepared from
commercial soap flakes) can be almost completely extracted by
chloroform but are much less soluble in ether; calcium stearate
was, however, only very slightly soluble in these solvents. HOL­
ROY has suggested that to ensure complete extraction of fatty
material in sewage sludges, without including the metallic com­
ponents, acid treatment with hydrochloric acid, which will hydro­
lyse the soaps to free fatty acids, followed by extraction with
petroleum, ethyl ether, or chloroform, gives consistent results
whichever solvent is used.

Soaps are found in sewage, sewage sludges (especially in sedi-
mentation tank sludge), laundry wastes, and textile wastes. Calci-
um soaps present in sewage and sewage sludge are formed by the
action of hard water, containing calcium salts, on sodium and
potassium soaps used for washing and cleaning purposes.
NATURE AND EFFECTS OF POLLUTION

Waxes are esters of higher fatty acids and either a monohydric solid alcohol (such as cetyl alcohol, \( \text{C}_{28} \text{H}_{55} \text{OH} \)), or a sterol (such as cholesterol, \( \text{C}_{27} \text{H}_{47} \text{OH} \)). A typical wax is spermaceti whose main component is cetyl palmitate, \( \text{C}_{36} \text{H}_{72} \text{COOC}_{16} \text{H}_{33} \). Synthetic waxes are known in addition to natural waxes. Naturally occurring waxes, such as lanoline found in wool, are usually complex mixtures. Waxes are present in waste waters from the scouring of wool and in certain paper and textile wastes.

So-called paraffin wax, although similar to waxes in certain physical properties, does not belong to the class of waxes but consists of a mixture of higher solid aliphatic hydrocarbons; it is used in the manufacture of candles and for waterproofing paper.

Carbohydrates are compounds of carbon, hydrogen, and oxygen, which are widely distributed in the animal and vegetable kingdom. They include the simple sugars, such as glucose, \( \text{C}_{6} \text{H}_{12} \text{O}_{6} \), and sucrose (cane sugar), \( \text{C}_{12} \text{H}_{22} \text{O}_{11} \), as well as the more complex polysaccharides having the general formula \( \text{(C}_{6} \text{H}_{10} \text{O}_{5})_{n} \), such as starch, dextrin, glycogen, alginic acid, and cellulose. Starch and dextrin are used in paper making and in textile printing, and are therefore sometimes found in paper and textile waste waters. Cotton, paper pulp, and artificial silk (rayon) consist largely of cellulose. The polysaccharides when boiled with dilute acids or subjected to the action of micro-organisms, are hydrolysed back to the simple sugars.

Resins (e.g. amber and common rosin) are complex compounds of carbon, hydrogen and oxygen found as secretions in many plants. Thus, when the exudation from various species of pine is steam-distilled, it yields a non-volatile ‘rosin’ and a volatile oil of turpentine. Resins on boiling with alkalis give resin soaps which are used in conjunction with resins in sizing paper to render it waterproof. Resins are also used in the manufacture of linoleum, in paint manufacture, in the textile industries, and in the preparation of lacquers.

Turpentine, which consists mainly of the hydrocarbon pinene, \( \text{C}_{10} \text{H}_{16} \), was formerly much used as a solvent for paints and varnishes, but as it has become very expensive in this country, it has been largely replaced by cheaper synthetic solvents (turpentine ‘substitute’).

Rubber is a polymerized form of the hydrocarbon isoprene and has the general formula \( \text{(C}_{5} \text{H}_{8})_{n} \). It is found in wastes from rubber manufacture and processing and from the waxing of paper.

Coal, which is made up of complex organic substances as well as some mineral matter, is present in finely divided form in effluents from coal-washing plants and is a common form of pollution in rivers in mining districts (see suspended matter, pages 40-41).
Oil as a form of river pollution may come from barges, tankers, and boats on rivers or canals, or may be derived from industrial wastes, metallurgical industries, engineering works, garages, or indeed any trade premises using lubricating oils or fuel oils, the commonest of which are the fairly high-boiling hydrocarbon oils derived from petroleum. These are lighter than water and often show a distinct greenish fluorescence especially when examined in ultra-violet light. As little as 0.001 μg of oil in a litre of well water (i.e. only 0.000001 p.p.m.) has been detected by a fluorescence test 18.

Oils obtained from coal-tar are usually slightly denser than water and are characterized by the presence of phenols (see Tar, page 25).

Oil is most objectionable in a stream not only from an aesthetic standpoint on account of the visible pollution it causes but also because it spreads to form a thin film on the surface and so tends to prevent diffusion of oxygen into the water, thus interfering with re-aeration of the river water. Recent experiments by Dowson and Truesdale 18a, show that oil films only have a marked effect on the absorption by water of the oxygen of the air when the film thickness is greater than \( 10^{-4} \) cm. Oil in any considerable amount also tends to coat the gills of fish, thus making the utilization of dissolved oxygen difficult or even impossible.

According to Hogg, Petter and Collett 11, a film of oil only about 0.000012 in. thick on water (corresponding to 1 gallon of oil dispersed over a water surface of about 4 acres) shows up as bright iridescent colours. Wax 12 has given interesting figures showing the relation between the thickness of an oil film, the appearance, and the quantity of oil present, assuming uniform distribution over the surface of the stream, and these are reproduced in Table 2.

<table>
<thead>
<tr>
<th>Approximate thickness of oil film (decimals of an inch)</th>
<th>Appearance of oil on surface of water</th>
<th>Approximate amount of oil for film 1 sq. mile in area (Imperial gallons)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0000015</td>
<td>Barely visible</td>
<td>21</td>
</tr>
<tr>
<td>0.0000030</td>
<td>Visible as silvery sheen</td>
<td>42</td>
</tr>
<tr>
<td>0.0000060</td>
<td>First traces of colour</td>
<td>83</td>
</tr>
<tr>
<td>0.0000120</td>
<td>Bright bands of colour</td>
<td>167</td>
</tr>
<tr>
<td>0.0000400</td>
<td>Colours begin to turn dull</td>
<td>555</td>
</tr>
<tr>
<td>0.0000800</td>
<td>Colours much darker</td>
<td>1,110</td>
</tr>
</tbody>
</table>

In addition to the water-insoluble oils, there are the so-called 'soluble' oils ('cutting' oils or 'degreasing' oils), used, for example, in engineering factories making aircraft engines. They can cause serious pollution in streams and difficulties in sewage treatment.
Cutting oils are homogeneous mixtures of oil emulsified in water with an emulsifying agent (e.g. sulphonated oils, alkali soaps) and a little cresol and alkali; they are largely used as coolants and lubricants wherever machining operations with high-speed tools are carried out. Degreasing oils (used for degreasing floors, etc.) are brown in colour with a pH ranging from 7-11; a typical example is a mixture of an organic solvent (chlorinated hydrocarbons, xylene) and a synthetic emulsifier (e.g. Teepol) which is heated with aqueous caustic soda to form a homogeneous mixture.

Although soluble oils somewhat resemble ordinary oils in certain respects, they have the objectionable property of giving stable milky emulsions on mixing with water.

There is growing concern about the pollution of the sea and of our beaches by oily wastes discharged from ships, a form of pollution which has increased since the replacement of coal by oil fuel. This is not only objectionable to bathers, but also causes much needless destruction of wild bird life. A report on the 'Prevention of pollution of the sea by oil' was published by the Ministry of Transport and Civil Aviation in 1953 and should be consulted by all who are interested in the subject.

Tar is a viscous dark brown or almost black liquid usually a little denser than water. Part of it may, however, float on the surface of water, particularly if entrained with floating suspended matter. Tar is produced by the destructive distillation of coal, peat, wood, bituminous shale and other naturally occurring organic materials. Its composition depends upon the nature of the material from which it is derived, the temperature of the distillation and other factors. It is a complicated mixture of organic substances and may contain simple and complex hydrocarbons (especially aromatic hydrocarbons), phenols, organic bases, etc. Tar is also produced as an unwanted by-product in the synthesis and preparation of many organic compounds.

The most important tar from a pollution standpoint is coal-tar, which is a valuable by-product in the manufacture of gas from coal. Coal-tar is characterized by the presence of appreciable quantities of phenols—hence the name 'tar acids' sometimes given to the mixture of phenols in tar. Tar, in view of its content of such toxic substances as phenols (e.g. phenol, the three cresols, naphthols, etc.) and organic bases (e.g. acridine, pyridine, quinoline, etc.), is an extremely dangerous form of pollution in a river and its presence causes destruction of bacteria, fish, and other aquatic life. It may also be harmful on account of its tendency to form a dark-coloured sticky film on the surface of a stream, thus preventing re-aeration and rendering the water objectionable from an aesthetic viewpoint.
Many thousands of organic compounds (e.g. hydrocarbons, alcohols, ketones, acids, amines, etc.) are prepared and used industrially and so may be present in waste waters from chemical and other factories. These compounds may be objectionable because they are toxic (see Toxic organic compounds, page 29) or on account of their tendency to undergo fermentation.

Organic acids (e.g. acetic acid) exhibit acid properties to a considerably lesser degree than the purely inorganic or mineral acids (page 30).

Dyes

Dyes in common use today are, with few exceptions, intensely coloured synthetic organic compounds capable of fixing themselves permanently to various materials, i.e. not removed by washing. They are prepared for the most part from such coal-tar hydrocarbons as benzene, toluene, the xylenes, naphthalene, anthracene, etc. Many thousands of such dyes have now been synthesized and they have practically displaced the older naturally occurring vegetable dyes. They find their most important application in the dyeing and printing of textiles (e.g. cotton, linen, silk, rayon, nylon, wool, etc.), but are also used to some extent for dyeing paper and leather, in the preparation of certain inks, and in photography.

Dyes usually contain characteristic groups ("chromophores" such as the nitro, $-\text{NO}_2$, azo, $-\text{N}==\text{N}-$, and carbonyl, $=\text{CO}$, groups) which confer colour on the molecule, and, in addition such auxiliary groups ("auxochromes") as the sulphonlic acid ($-\text{SO}_2\text{H}$), carboxyl ($-\text{COOH}$), amino ($-\text{NH}_2$), dimethylamino ($-\text{N(CH}_3)_2$), and hydroxyl ($-\text{OH}$) groups, which aid in solubilizing the dye and assist in its attachment to the textile fibre. Some dyes only adhere permanently to textile fibres when used in conjunction with mordants (e.g. salts of chromium, aluminium, iron, tin, etc.) with which the dye forms an insoluble coloured lake.

Dyes are usually present only in small amounts in textile waste waters but may be objectionable on account of their colour. The question of colour is discussed under the heading of Physical pollution (see page 36).

Synthetic detergents

These compounds have caused much concern during the past few years owing to their tendency even in small amounts to cause foam on rivers (see under Physical pollution, page 41). But there is considerable experimental evidence that low concentration of synthetic detergents are toxic to fish. Thus, Dexxas and his co-workers have shown that concentrations of only 5 p.p.m. of some
anionic and non-ionic synthetic detergents can kill certain fish in 5–100 hours though certain species can to some extent become acclimatized to the detergents. Leclerc and Devlaminc14 have compared natural detergents (soaps) with synthetic detergents as regards their toxicity towards fish and some of their results are reproduced in Table 3.

Table 3. Toxicity of natural and synthetic detergents to fish in distilled water and in hard water

<table>
<thead>
<tr>
<th>Detergent Type</th>
<th>Minimum lethal concentration expressed as p.p.m. of active product</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>In distilled water (hardness = 244 p.p.m. of CaCO₃)</td>
</tr>
<tr>
<td><strong>Natural detergents</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium palmitate</td>
<td>10-12</td>
</tr>
<tr>
<td>Sodium stearate</td>
<td>10-12</td>
</tr>
<tr>
<td><strong>Synthetic detergents</strong></td>
<td></td>
</tr>
<tr>
<td>Sodium lauryl sulphate (anionic)</td>
<td>6-7</td>
</tr>
<tr>
<td>Sodium dodecyl benzenesulphonate (anionic)</td>
<td>6-7</td>
</tr>
<tr>
<td>Polyglycol ether (non-ionic)</td>
<td>2-3</td>
</tr>
</tbody>
</table>

It will be seen that whilst the natural detergents exhibit very greatly reduced toxicity in hard water (due to their precipitation as insoluble calcium salts), the synthetic detergents show the same toxicity in distilled water and in hard water.

Water plants, as well as water animals, can be adversely affected by synthetic detergents. Laboratory experiments14a,14b (using Santomerse, a detergent of the alkyl aryl sulphonate type) have shown that the rooted plants Ranunculus aquatilis, Potamogeton pectina tus, and Potamogeton denius are unable to grow in 2-5 p.p.m. of the detergent and Ranunculus is much affected even by as little as 1 p.p.m. Addition of anti-foam agents does not reduce the toxicity of the detergent towards these plants. The alga Cladophora and the moss Euryynchium, however, grow satisfactorily even in as much as 3 p.p.m. of the detergent.

One tragicomic, though unexpected, result of pollution caused by synthetic detergents has been reported15 in the U.S.A. where mortality amongst ducks has occurred in certain waters receiving sewage containing synthetic detergents. The normal protective oily coating on duck feathers tends to be dissolved by synthetic detergents, thus causing the feathers to become waterlogged and the ducks to be drowned!
Table 4. Some important organic compounds toxic to fish and present in trade wastes discharging to streams.

(See also Table 35, Chapter 7)

<table>
<thead>
<tr>
<th>Class</th>
<th>Typical examples</th>
<th>Occurrence</th>
<th>Approximate lethal concentration to fish p.p.m.</th>
<th>References (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenols</td>
<td>Phenol, C₆H₅OH; Cresols, m-, p-, and o-C₆H₅(CH₃)OH</td>
<td>gas works effluents; coal-tar; chemical wastes; synthetic resin wastes</td>
<td>1–10</td>
<td>16, 17, 18, 19</td>
</tr>
<tr>
<td>Tar bases</td>
<td>Pyridine, C₅H₅N</td>
<td>gas works effluents</td>
<td>1,000</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Acridine, C₅H₅N⁺</td>
<td>coal-tar</td>
<td>0–1</td>
<td>16, 20</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>Naphthalene, C₁₀H₈</td>
<td>gas works effluents; coal-tar</td>
<td>10–20</td>
<td>18, 19, 20</td>
</tr>
<tr>
<td>Aldehydes</td>
<td>Formaldehyde, H–CHO</td>
<td>synthetic resin wastes; penicillin wastes</td>
<td>50 (kills trout in 1–3 days)</td>
<td>21</td>
</tr>
<tr>
<td>Cyanogen compounds</td>
<td>Cyanides, e.g. KCN, NH₄CN</td>
<td>plating wastes; gas liquor</td>
<td>0.04–0.1* (as CN)</td>
<td>16, 22, 23</td>
</tr>
<tr>
<td>Chlorinated hydrocarbons</td>
<td>DDT, CI–C₆H₅(CH–CCl₃)</td>
<td>insecticidal sprays; wastes from manufacture of insecticides</td>
<td>&gt;0.1 (toxic to goldfish)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>CI–C₆H₅(CH₂Cl₂)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(dichloro-diphenyl-trichloroethane)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Gammaclone, IC₆H₅Cl₆</td>
<td></td>
<td>0.005</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>(γ-hexachloreuclohexane)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mercaptans</td>
<td>Methyl mercaptan, CH₃SH</td>
<td>wood pulp wastes (sulphate process); oil refinery wastes</td>
<td>1 (kills game fish in 2–6 h)</td>
<td>27</td>
</tr>
</tbody>
</table>

* According to Herning’s extrapolation of a log-concentration/log-median survival time curve obtained in experiments on the effect of potassium cyanide on rainbow trout shows that the threshold concentration as 17°C is 0.023 p.p.m. (expressed as CN). Presumably therefore, concentrations of cyanide somewhat below this value can be regarded as ‘safe’ for the fish.
**NATURE AND EFFECTS OF POLLUTION**

**Toxic organic chemicals**

Many trade wastes (e.g. wastes from the manufacture of coal gas, organic chemicals, and insecticides) contain poisonous organic compounds (such as phenols, tar bases, cyanides, and DDT) which not only have the objectionable property of killing bacteria and so rendering a river sterile and unable to undergo self-purification, but also in quite low concentrations can cause mortality amongst fish and other aquatic life. Some of these compounds have already been mentioned earlier in this chapter (e.g. phenols, page 22; synthetic detergents, page 26). Often one of the earliest indications of the contamination of a river by such toxic compounds is the presence of dead or dying fish. Typical examples of toxic organic compounds are shown in Table 4 (cf. also Table 35, Chapter 7). Owing to the many experimental difficulties involved in determining with even moderate accuracy the toxicity of substances to fish, it must be emphasized that the results given in the table for the lethal concentration of the various substances to fish are approximate and are intended merely as a rough guide to the order of magnitude of the figure. The table does reveal the rather surprising thing that the merest traces of some compounds (e.g. cyanides) are fatal to fish. According to Southgate (22), cyanide is toxic to trout in a concentration as low as about 0.04 p.p.m. (expressed as CN). Cyanides have been responsible in recent years for much mortality amongst fish in many rivers in this country. The effects of toxic compounds upon fish are of such importance that the subject will be more fully discussed in a later chapter (see Chapter 7).

**Effects of pollution by organic matter**

The various organic compounds and materials so far discussed can, with few exceptions, be broken down by micro-organisms present in river water, and dissolved oxygen is used up in these reactions. Even toxic substances, such as phenols and cyanides, can suffer breakdown in this way, provided that they are present in sufficiently low concentrations. Indeed, much evidence is accumulating to show that bacteria can become acclimatized to toxic substances (cf. page 515).

If the organic pollution load is small and the dilution by well-oxygenated stream water is high, sufficient dissolved oxygen may be present to enable certain bacteria—aerobic bacteria which require free oxygen—to break down the organic matter completely to relatively harmless and odourless end-products. The river thus recovers naturally from the effects of pollution and is said to have undergone ‘self-purification’. The oxidation reactions which occur are as follows:
ASPECTS OF RIVER POLLUTION

C\textsuperscript{+}→CO\textsubscript{2} and normal and bi-carbonates
H→H\textsubscript{2}O
N→nitrates (e.g. NaNO\textsubscript{3})
S→sulphates (e.g. Na\textsubscript{2}SO\textsubscript{4})
P→phosphates (e.g. Na\textsubscript{2}HPO\textsubscript{4})

Often, however, massive pollution by organic matter causes exhaustion of the dissolved oxygen. The remaining organic matter is then broken down by a different set of bacteria—the anaerobic bacteria which do not require free oxygen but can utilize combined oxygen in the form of nitrates, sulphates, phosphates, organic compounds, etc. Putrefaction then occurs, resulting in the breakdown of organic matter to a different set of end-products, some of which (e.g. organic amines, organic sulphur compounds, sulphuric hydrogen, phosphine, etc.) have objectionable odours and may be the cause of complaints:

C→CH\textsubscript{4}

methane

N→NH\textsubscript{3} and organic amines

ammonia

S→H\textsubscript{2}S and organic sulphur compounds

hydrogen sulphide

P→PH\textsubscript{3} and organic phosphorus compounds

phosphine

If fish are present in a river receiving a heavy organic load, there may be mortality when the dissolved oxygen falls below a certain critical level—in the case of many fish this is about 57 per cent of saturation, or about 5 p.p.m. of dissolved oxygen (see page 110).

INORGANIC OR MINERAL POLLUTION

Acids and Alkalis

Many industrial wastes contain corrosive inorganic acids or alkalis which can do extensive damage to a stream by breaking down its natural buffer system and altering its normal pH value. Typical examples of such waste waters are shown in Table 5 from which it will be seen that many of the alkaline wastes have pH values up to 12 or even higher whilst the acid wastes frequently go down to pH 1 or less.

* Part of the carbon is always transformed to insoluble “humus” (page 142).
### Table 5. Some typical alkaline and acid waste waters

<table>
<thead>
<tr>
<th>Alkaline Wastes</th>
<th>pH</th>
<th>Alkali(s) present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas liquor</td>
<td>8–9</td>
<td>Ammonia</td>
</tr>
<tr>
<td>Kier liquor (kiering of cotton or straw)</td>
<td>12–14</td>
<td>Caustic soda, sodium carbonate, lime</td>
</tr>
<tr>
<td>Cotton mercerizing wastes</td>
<td>12–14</td>
<td>Caustic soda</td>
</tr>
<tr>
<td>Chemical manufacturing wastes</td>
<td>variable</td>
<td></td>
</tr>
<tr>
<td>Tannery wastes</td>
<td>up to 12</td>
<td></td>
</tr>
<tr>
<td>Wood scouring wastes (untreated)</td>
<td>9–10</td>
<td>Lime, Sodium carbonate</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Acid Wastes</th>
<th>pH</th>
<th>Acid(s) present</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mine water</td>
<td>2.5–6.5</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Battery factory wastes</td>
<td>1–0 or less</td>
<td>H₂SO₄, sometimes HCl, rarely H₃PO₄</td>
</tr>
<tr>
<td>Iron pickle liquor</td>
<td>strongly acid</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Copper pickle liquor</td>
<td>strongly acid</td>
<td>H₂SO₄, sometimes HCl, rarely H₃PO₄</td>
</tr>
<tr>
<td>DDT wastes</td>
<td>very strongly acid</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Viscose rayon wastes</td>
<td>strongly acid</td>
<td>H₂SO₄, Sulphurous acid (H₂S₂O₇)</td>
</tr>
<tr>
<td>Wood pulp spent sulphite liquor</td>
<td>2–4</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>Chemical manufacturing wastes</td>
<td>variable</td>
<td>H₂SO₄, HCl, HNO₃, H₃PO₄</td>
</tr>
<tr>
<td>Munition factory wastes</td>
<td>1–3</td>
<td>H₂SO₄, HNO₃</td>
</tr>
<tr>
<td>Wood scouring wastes (cracked) with acid</td>
<td>&lt;4</td>
<td>H₂SO₄</td>
</tr>
</tbody>
</table>

Acids are particularly objectionable in a stream on account of the corrosion they may cause to metal or concrete structures, pumps, etc., especially if the pH value of the stream falls below about 5.0. They may also liberate evil-smelling sulphuretted hydrogen from sludge deposits and river mud. Acids and alkalis can destroy bacteria and other micro-organisms and so inhibit or even prevent self-purification of a stream, they are also lethal to fish and other forms of aquatic life. According to Roberts, Grindley and Williams, freshwater fish usually thrive in waters having pH values lying between 5-0 and 8-5 but certain species are affected by more acid or alkaline conditions. In particular, fish are liable to be adversely affected if suddenly transferred from an alkaline stream to an acid stream or vice versa.
Toxic inorganic compounds

The commonest toxic inorganic substances are free chlorine, ammonia, sulphydryl hydrogen and soluble sulphides, and the salts of many heavy metals (e.g. copper, zinc, lead, nickel, vanadium, etc.). Any appreciable amounts of these compounds may hinder or even prevent self-purification of rivers (see Chapter 6, page 143) and may kill fish and other aquatic life whether animal or vegetable. According to Fair and Whipple 28, the concentrations of copper sulphate that will kill trout, perch and black bass are 0.14, 0.75 and 2.1 p.p.m. respectively. Many algae are destroyed by quite minute doses of copper sulphate. Fair and Whipple 28 state that some blue-green algae are killed by as little as 0.1 p.p.m. of copper sulphate whilst other algae may require 10-20 times this dose for destruction. A striking example of the devastating effect of traces of copper on biological life in streams is given by Butcher 29. He showed that effluents discharging to the River Churnet from a copper works (giving a copper concentration of 1-2 p.p.m. in the river) completely exterminated all animal life for a distance of over 10 miles, and even sewage fungus was absent or very rare and algae were extremely rare.

Zinc is another heavy metal that is very toxic to fish. Schott 30 has reported that, owing to an increase in the free carbon dioxide of the water supply to fish tanks containing trout, sufficient zinc was dissolved from newly galvanized pipes to give a zinc concentration of 0.15 p.p.m. which proved fatal to the fish. The author has experience of a number of cases of mortality amongst fish caused by the presence of traces of zinc in solution. On one occasion when some unwanted old smoke bombs containing zinc carbonate were dumped into a lodge, sufficient zinc (1-2 p.p.m.) passed into solution to cause the death of many coarse fish in the lodge. Many industrial effluents (e.g. viscose rayon wastes, wastes from rubber factories, wastes from the manufacture of zinc compounds) contain considerable quantities of zinc.

Metallic contamination in a stream, especially arsenic and lead, may constitute a danger to public health if the water is to be used subsequently for drinking purposes. The U.S. Public Health Service has fixed maximum desirable limits for these and other common toxic metals in drinking water (cf. Chapter 5, page 99).

It is only within comparatively recent years that fluorides have been recognized as toxic substances. In view of the increasing commercial manufacture and use of chemicals, refrigerants, plastics, insecticides, and other materials containing fluorine, many more industrial effluents will contain fluorides. Rivers containing fluoride-bearing wastes may be a hazard to public health if the
water is to be used for domestic supplies. Whilst it has been demonstrated that fluoride up to about 1 p.p.m. (expressed as F) is necessary in drinking-water to prevent decay of teeth, amounts greater than about 1.5 p.p.m. (expressed as F) are liable to cause dental fluorosis or 'mottled enamel' and the teeth become brittle and deteriorate. The maximum desirable level of F in potable water has therefore been fixed at 1.5 p.p.m. by the U.S. Public Health Service (page 99) and if the amount exceeds this figure the river water must be treated to reduce the F content to about 1 p.p.m. (e.g. by ion exchange with granular calcium phosphate). Little information is available on the toxicity of fluorides to fish, but according to Southgate experiments at the Water Pollution Research Laboratory have shown that sodium fluoride in a concentration of 358 p.p.m. (as F) is toxic to rainbow trout in softened water. Fluorides are, therefore, only moderately toxic towards fish.

Many inorganic gases are very toxic to fish. Table 6, compiled from a review by Doudoroff and Katz, gives the toxicity of some common gases in aqueous solution:

<table>
<thead>
<tr>
<th>Gas</th>
<th>Formula</th>
<th>Approximate toxic concentration to fish p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen sulphide</td>
<td>H₂S</td>
<td>0.5-1.0</td>
</tr>
<tr>
<td>Chlorine</td>
<td>Cl₂</td>
<td>0.05-0.2</td>
</tr>
<tr>
<td>Ozone</td>
<td>O₃</td>
<td>0.1-1.0</td>
</tr>
<tr>
<td>Phosphine</td>
<td>PH₃</td>
<td>about 3-6</td>
</tr>
</tbody>
</table>

A considerable amount of work has been done on the experimental determination of the toxicity of various substances towards fish and attempts have been made to express the results in terms of a threshold concentration or minimum lethal concentration. Doudoroff and Katz have, however, sounded a note of warning by pointing out that the minimum harmful or lethal concentration of a toxic compound is not necessarily a fixed quantity but may vary greatly with the experimental conditions; important factors in this connection are the duration of the experiment, the chemical composition of the water (hardness, dissolved oxygen content, etc.), the temperature, the concentration of other substances having either a synergistic (additive) or an antagonistic effect, and the

* Hydrogen sulphide is very objectionable not only on account of its toxicity to fish but also because of its offensive odour (page 53), its property of blackening lead paints and materia made of copper and brass, and its tendency to cause corrosion of concrete structures (see page 53).
species and age of the fish. A similar view is taken by Inoue in a discussion of the many conditions affecting the toxicity of poisonous substances towards living organisms. He concludes that a change in such factors as temperature, pH, the concentration and nature of other ions, the type of organism and its previous environment, and the concentration of food, can alter the toxicity very considerably.

Salts of heavy metals appear to bring about the death of fish by coagulating the mucus around the gills with the result that the fish are asphyxiated. Certain metals (e.g. zinc) are much more toxic to fish in soft waters than in hard waters. These and other matters relating to fish and pollution, are discussed in more detail in the chapter on fish (see Chapter 7).

It is important to remember that the effect of toxic substances on fish food may be a vital factor in determining whether fish can flourish or survive in a polluted stream, as in many cases the lower organisms upon which fish depend for food are even more susceptible to a particular poison than are the fish themselves. For instance, water fleas (Daphnia magna) are adversely affected by as little as 0·1 p.p.m. of Cr (present as sodium chromate) whereas the lethal dose of chromate for fish is at least 20 p.p.m. (cf. Table 35, Chapter 7; also Table 60, Chapter 9).

Soluble salts
Soluble salts (or dissolved solids) commonly found in streams and in discharges to streams include chlorides, sulphates, nitrates, bicarbonates, and phosphates of sodium, potassium, calcium, magnesium, iron, and manganese. In small concentrations these are harmless to freshwater fish. Drainage from a salt works, and brine from water softening plants using ion-exchange methods of softening, are, however, liable to contain large amounts of sodium chloride which may pollute a freshwater stream by converting it to a brackish water or even a salt water unsuitable for certain fish and vegetation. Krul and Liefrink have given a classification of waters according to their salt content and this is shown in Table 7; for comparison it may be noted that sea water contains about 20,000 p.p.m. of Cl.

<table>
<thead>
<tr>
<th>Description of water</th>
<th>Content of salt expressed as p.p.m. of Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh water</td>
<td>up to 100</td>
</tr>
<tr>
<td>Brackish water</td>
<td>100-1,000</td>
</tr>
<tr>
<td>Salt water</td>
<td>over 1,000</td>
</tr>
</tbody>
</table>
According to Roberts, Grindley and Williams, freshwater weeds (e.g. blanket weed) die rapidly in a stream containing 1,000 p.p.m. of Cl, but certain freshwater fish (e.g. perch) are able to live in water containing as much as 2,000 p.p.m. of Cl. The cause of mortality of many freshwater fish in salt water is doubtless an osmotic phenomenon; indeed, Ellis states that any effluent (e.g. brine wastes) with an osmotic pressure above 6 atm. will kill freshwater fish.

Certain soluble salts (e.g. the bicarbonates, sulphates and chlorides of calcium and magnesium) are harmful in more than small concentrations in river water because they render the water hard and consequently unsuitable for many industrial processes. For steam raising, it is particularly important to eliminate these salts by softening the water, otherwise hard scale may form inside the boiler, thus leading to decreased efficiency or even to bursting of the boiler.

Effluents having an excessive content of soluble salts may also be objectionable in a stream because they are liable to cause corrosion of pumps, pipelines and other structures made of metal or concrete. Sulphates are particularly objectionable in this respect since they can be reduced to sulphides which by oxidation at air level give corrosive sulphuric acid, or they can also act directly on concrete and cause rapid deterioration. BEVAN gives the following as a rough guide to the direct action of sulphates on concrete:

<table>
<thead>
<tr>
<th>Sulphate content of water (p.p.m. of SO$_3$)</th>
<th>Action on concrete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Up to 300</td>
<td>None or slow</td>
</tr>
<tr>
<td>300–1000</td>
<td>Moderately severe</td>
</tr>
<tr>
<td>Over 1000</td>
<td>Rapid</td>
</tr>
</tbody>
</table>

These figures apply to the more vulnerable lean concretes cast in situ; in the case of the denser and more resistant Portland cement concretes, or asbestos cements, however, the action of sulphates only becomes at all marked when the SO$_3$ concentration reaches 1000 p.p.m. over any considerable period of time.

Soluble salts of certain relatively non-toxic metals (e.g. iron, aluminium) may cause pollution in a river by reacting with the natural bicarbonate alkalinity to give precipitates of insoluble hydroxides. This is particularly objectionable in the case of iron, since ferric hydroxide has a reddish-brown colour and forms an unsightly deposit on the stream bed (cf. page 37). Some river boards have a standard for protecting the river from this kind of pollution (see Chapter 14).
ASPECTS OF RIVER POLLUTION

Inert insoluble inorganic substances

Many inert insoluble inorganic materials, such as clay, chalk (CaCO₃), gypsum, etc., are sometimes present in trade wastes (e.g. in paper making effluents). They are undesirable in a stream because they increase its turbidity (page 37) and its suspended matter content (page 40).

PHYSICAL TYPES OF POLLUTION

COLOUR

Many trade wastes discharging to a river have a pronounced colour which they may impart to the river. The colour is due in most cases to organic dyes (page 26) but there are some highly coloured substances of mineral origin, especially compounds of iron and chromium.*

The layman often judges the condition of a sample by its colour, but the colour of a waste water is not necessarily a safe guide to its polluting power and this was recognized by the law (e.g. the 1876 Act, page 5) which until recently permitted so-called 'innocuous discoloration' in trade effluents. No manufacturer, of course, deliberately wants to waste his valuable dyes but unfortunately mere traces of many organic dyestuffs can impart a distinct colour to water without otherwise materially affecting its quality. For example, a solution of the dyestuff magenta shows a distinct reddish colour at as low a concentration as 1 in 50,000,000 parts of water (i.e. 0·02 p.p.m.). Again, the substance fluorescein still exhibits its characteristic yellow-green fluorescence by reflected light in a solution containing only 1 in 40,000,000 parts of water (i.e. 0·025 p.p.m.). Such small amounts of discoloration cannot be detected by ordinary chemical methods of assessing pollution. The intense fluorescence of fluorescein finds application in the detection of any pollution of waters by sewage or trade wastes and for tracing the course of underground streams.

When it is considered desirable to remove colour from waste waters discharging to streams, this can often be achieved by coagulation with chemicals (see page 509) thereby at the same time removing any finely divided suspended matter and colloidal organic matter, and reducing the oxygen demand of the waste. Activated carbon is often very effective in reducing or removing the colour of a waste but unfortunately fairly large amounts are required which makes its use expensive.

Under the Rivers (Prevention of Pollution) Act, 1951, the control

* Chromium, in fact, derives its name from the Greek word, chrosa, colour.
of colour in a discharge can be achieved by means of a special by-

law which must be confirmed by the Minister. The difficulties of
framing such a by-law are, however, great in view of the many
complications involved in defining a particular colour precisely and
in deciding what intensity of colour shall constitute pollution.

Colour in itself is not necessarily harmful. Rivers draining peaty
land and containing so-called 'humic acids' of vegetable origin are
often highly coloured. Many streams in this country supporting
good fish populations have quite a brown colour.

Interaction between two different trade wastes in a stream, or
between a trade effluent and substances present naturally in stream,
can sometimes produce quite an intense coloration. One example
of this is the reaction between mine water and the natural bicarbon-
ate alkalinity of a river to give an unsightly reddish-brown opal-

cence and eventually a deposit of ferric hydroxide, $\text{Fe(OH)}_3$; if
the stream is devoid of dissolved oxygen the water may turn black
owing to formation of ferrous sulphide. Again, gas liquor and
trade wastes containing iron can yield intense colours (red, brown,
purple, etc.) due to formation of coloured iron compounds with
phenols (especially phenols containing 2 hydroxyl groups in the
ortho position), thiocyanates, etc., present in gas liquor. Red-
lich\textsuperscript{37} has pointed out that wastes from tanneries using the vege-
table tan process may cause deep green or inky-blue colorations
or precipitates if discharged to iron-containing streams owing to
interaction of tannins with iron.

TURBIDITY

A striking physical characteristic of sewage and of most industrial
waste waters is their degree of cloudiness or 'turbidity' which is
caused in the main by the presence either of colloidal matter or of
very finely divided suspended matter which settles only with difficulty.
Matter in the colloidal state differs from coarse suspensions
chiefly in its particle size, colloids being intermediate in dimensions
between molecules and coarse suspensions. Thus, roughly, the
following classification can be used:

- **True solutions** (molecules and ions) . . . . Particle size <1 m\textmu
- **Colloidal solutions** (molecular aggregates) . . . . Particle size 1-100 m\textmu
- **Suspensions** (coarse particles) . . . . Particle size >100 m\textmu

$(1 \text{ m\textmu} = 0.000001 \text{ mm} = \text{about 0.00000004 in.})$

Colloidal particles are too small to be retained by ordinary filter
paper, they do not settle on standing, and they cannot be seen with
an ordinary microscope (whose limit of vision is about 100 μm). There is, of course, no sharp line of demarcation between colloidal particles and suspensions. Matter having a particle size in the region of 100 μm is often referred to as ‘pseudo-colloidal’ and has properties intermediate between those of colloids and suspensions, e.g. it does settle on standing but only extremely slowly.

As a rule, the more pronounced the turbidity, the stronger is the sewage or trade waste and the worse is its effect upon a river. The degree of turbidity of a stream water is, therefore, often taken to be an approximate measure of the intensity of the pollution. Indeed, Ries has shown that measurements of changes in the turbidity of rivers can be used to evaluate the effects of pollution by waste waters and even to follow the course of self-purification of streams. In this connection, however, two reservations must be made. In the first place, a river water might be somewhat turbid owing to the presence of small amounts of some inert and relatively harmless material (e.g. clay), and yet be satisfactory as a fishing stream and for most other purposes. Indeed, Roberts, Grindley and Williams state that turbidity has no direct effect upon fish and that many of the best fishing streams in the world are turbid; they do, however, add that turbidity by cutting off some sunlight does reduce the amount of plant life in a stream. Secondly, it must be emphasized that the absence of turbidity does not necessarily imply that a stream is unpolluted for the clearest water might well be heavily contaminated with acids or toxic metals which do not cause turbidity.

Turbidity in water used for domestic purposes is very objectionable particularly if it is due to the presence of iron, which in quantities of 1 p.p.m. or more causes a brownish or reddish-brown opalescence eventually depositing as ferric hydroxide.

\[ \text{TURBIDITY} \]

The discharge of heated trade effluents from factories and mills and of large volumes of warm 'cooling water' from electricity generating stations may easily cause a temperature rise of several degrees in a river or canal. This can have a number of deleterious effects which are discussed at some length in a Government Report. When a rise in temperature occurs in a stream polluted by organic matter, there is not only disappearance of dissolved oxygen, due to the lower solubility of oxygen at the higher temperature, but also an increased rate of utilization of dissolved oxygen by biochemical reactions which proceed much faster at higher temperatures. For these reasons many rivers may be satisfactory as regards dissolved oxygen content in the winter but may contain little or none during
the summer. If the dissolved oxygen does fall to zero, putrefaction of organic matter will occur giving rise to bad smells and nuisance. Fish are affected by rise in temperature and there may even be mortality amongst those fish sensitive to temperature. Experiments reported by the Yorkshire Ouse River Board on fish survival in relation to temperature have shown that roach were not able to withstand for long periods water temperatures greater than about 27°C and that rainbow trout died when the water temperature was much above 18-19°C. Table 8 gives temperatures lethal to various kinds of fish when they were brought to these temperatures gradually; the figures are taken from the Government Report already mentioned.

<table>
<thead>
<tr>
<th>Fish</th>
<th>Temperature at which fish can live for prolonged periods °C</th>
<th>Lethal temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Trout</td>
<td>22</td>
<td>25</td>
</tr>
<tr>
<td>Pike</td>
<td>27</td>
<td>30</td>
</tr>
<tr>
<td>Goldfish</td>
<td>30</td>
<td>35</td>
</tr>
</tbody>
</table>

Although fish can become acclimatized to high temperatures, it is important to realize that the sudden transference of fish to a warm water may result in death at a lower temperature than that given above. Thus, Patrick has reported that a sudden change in temperature of more than 2°C is harmful to the American sunfish. Furthermore, a temperature rise may have adverse effects on the hatching of the eggs of fish. A rise in temperature also has the unfortunate result of increasing the lethal effect of compounds toxic to fish; thus, according to the Government Report mentioned above, a temperature rise of 10°C doubles the toxicity of potassium cyanide to fish. Moreover, although a rise in temperature lowers the dissolved oxygen content of a stream, yet the minimum critical concentration of dissolved oxygen for fish is unfortunately greater when the temperature increases. Also, according to Ruttmann, the oxygen consumption of aquatic fauna nearly doubles itself for each 10°C rise in temperature. The conclusion seems to be that all these factors taken in the aggregate may mean that even a rise of a mere 1°C might have marked bad effects on fish life. The whole subject of pollution of a fishing stream by hot water is a complex one with a large number of variables, and it is therefore desirable that much further work be carried out on the problem so as to gain more precise information about the effect of temperature on fish.
Another harmful consequence of a discharge of warm water is that it tends to encourage excessive growths of 'sewage fungus' (see page 60) and of water weeds which may in some cases interfere with stream flow and so cause flooding.

The pollution of rivers by heated effluents or by hot water from electricity generating stations represents, of course, so much wasted heat. At most power stations, expensive cooling towers are provided (cf. page 102) for the purpose of lowering the temperature of the hot water before it discharges to the river. At the Battersea Power Station, London, an attempt has been made to utilize the waste heat by piping the hot water across the River Thames to heat blocks of flats in Pimlico. Owing to the high cost of the necessary piping this is only an economic proposition where there is sufficient density of population.

Under the Rivers (Prevention of Pollution) Act, 1951, it is possible to lay down a standard for temperature in the case of any new discharges to a river, but the Ministry of Housing and Local Government has appellate jurisdiction. Existing discharges can only be dealt with by means of a by-law for temperature which requires confirmation by the Minister. Thus, in either case, the result is that the Minister has the overriding decision.

SUSPENDED MATTER

Matter in suspension is one of the commonest forms of pollution, being present in sewage and in the majority of industrial waste waters. Its removal is of the utmost importance and can generally be carried out quite easily in settling tanks of suitable capacity and design (see Chapters 12 and 13).

Suspended matter can be mainly inorganic or 'mineral' in character, predominantly organic or 'volatile', or, as is commonly the case, partly inorganic and partly organic. The suspended matter in sewage effluents, dairy wastes and many coal washery effluents is largely organic in nature. On the other hand, wastes from sand-washing, china-clay works, and stone quarrying contain chiefly inorganic suspended solids. Such inert inorganic materials as talc (a magnesium silicate), china clay (or kaolin, an aluminium silicate), chalk (CaCO₃), gypsum (CaSO₄), titanium dioxide (TiO₂), zinc sulphide (ZnS), barium sulphate (BaSO₄), etc., are often used in conjunction with an organic binder (e.g. starch or casein) for filling and coating paper to give it a smooth surface, and so can occur as suspended matter in paper-making wastes. Paper pulp, which is also sometimes found in paper-making wastes, is largely organic in nature since it consists of cellulose (page 23).

The Royal Commission on Sewage Disposal in its 8th Report,
recommended that a sewage effluent discharging to a stream where
the dilution was at least eightfold should not have a suspended solids
content greater than 30 p.p.m. Superficially this may appear to
be a rather low figure, especially to a harassed sewage works manager
having an overloaded works, but a simple calculation will show that
even a Royal Commission effluent having just 30 p.p.m. of sus­
pended matter can cause deposition of quite a large amount of
solid matter in a stream. Thus, 1,000,000 gallons of such an effluent
discharging daily to a river would mean 300 lb. of suspended dry
solids per day, or very nearly 1 ton of solid matter every week!

Suspended solids containing much organic matter tend, especially
in warm weather, to undergo putrefaction in a river as a result of
which solids buoyed up by gas may rise to the surface, leading to
the formation of floating masses of evil-smelling sludge. Mineral
suspended solids are also objectionable as they may be deposited on
the bed, particularly if the stream is slow-moving. They may cause
silting up of the stream, and, if of a gritty character, may have an
abrasive action on pumps. Deposition of insoluble matter on a
stream bed may well lead to destruction of plant and animal life
and therefore of the natural food supplies of fish. Suspended solids
may have other injurious effects on fish life in a stream. If the sus­
pended matter is at all gritty, it may tend to choke the gills of the
fish, or even cause mechanical injury. Certain conditions of acidity
may liberate toxic metals in a soluble condition from suspended
matter contaminated by metallic compounds and so lead to fish
mortality. In streams containing trout and other game fish, de­
posits on the bed are particularly harmful since, according to
Roberts, Grindley and Williams 16, they foul the interstices in the
gravel of the bed and thus render the bed unsuitable for spawning.
Patrick 41 states that fish eggs can become buried by suspended
solids and that the pressure caused by the weight of solids may even
cause the less resistant eggs to burst!

Among the most objectionable effluents containing suspended
solids are coal washery waste waters. These are black and opaque
with much coal-dust, shale and dirt in suspension. They dis­
colour a stream and render it unfit for most uses. Pumps may be
damaged by abrasion, the bed of the stream may become silted up
and its banks blackened, vegetation may be injured and fish
destroyed.

**FOAM OR FROTH**

Foam consists of a suspension or dispersion of gas bubbles (usually
air) in a liquid medium (usually water). Many substances are
known to cause foam in water, for instance soaps and other deter­
gents, fish glue, and saponins. Scum and froth on the surface of
Rivers have been known for a considerable time, being especially noticeable in streams containing untreated alkaline organic discharges from paper mills making pulp from straw and other similar raw materials. But the present widespread complaints of masses of foam on rivers and at sewage treatment plants are of more recent origin, dating from the increasing use of synthetic detergents ('surface active agents') as cleansing agents in place of soap since World War II. Such names as Tide, Daz, Dref, Fah, Wok, Surf, Stergene, Thaw, Teepol, Spel, Cascade, Omo and many others are now becoming familiar household words.

LUMB has defined synthetic detergents as 'cleansing agents, other than soap, derived from organic chemicals'. They are often referred to as 'soapless washing powders' though a few are difficult to obtain in solid condition and so are sold in liquid form. The commercial preparations sold for household purposes are usually mixed with other substances in order to improve detergent action, e.g. sodium tripolyphosphate and other phosphates, sodium sulphate, sodium carbonate, sodium perborate and sodium silicate.

There is little doubt that these detergent preparations have come to stay since they not only have properties of value for domestic purposes but they also find considerable industrial use on account of their remarkable wetting, dispersing and emulsifying powers (for instance, in the leather, paper and rubber industries; in laundries; in the textile industries; and for bottle washing in breweries and dairies).

According to MANGANELLI, the sale of synthetic detergents in the U.S.A. was only 1 per cent of that of soap in 1941 whereas ten years later this figure had risen to 54 per cent. The production of these detergents in the United Kingdom has also undergone a phenomenal increase, having risen from a negligible figure in 1941 to about 10,000 tons in 1948. Much of the increasing popularity of synthetic detergents is undoubtedly due to the fact that, unlike soap, they are unaffected by hard water—hence their higher consumption and the greater number of complaints of froth in hard water areas. Synthetic detergents have the further advantage over soap that they can be used in acid solutions.

Many hundreds of synthetic detergents have been prepared and they can conveniently be classified into three main groups based upon their behaviour on ionization in aqueous solution:

(i) Anionic detergents—These ionize in aqueous solution giving a negatively charged group or anion (e.g. R·O·SO₃⁻ where R is a long hydrocarbon chain such as CH₃(CH₂)ₙ—) and a positively charged ion or cation which is usually sodium. Examples are sodium alkyl sulphates (e.g. Dref and Teepol)
and sodium alkyl aryl sulphonates (e.g. Santomerse). Most of the popular domestic detergent powders (e.g. Tide and Daz) belong to the group of alkyl aryl sulphonates. The long hydrocarbon chain in all these compounds is often termed ‘hydrophobic’ (or water-repelling), whilst the sulphate and sulphonate groupings are ‘hydrophilic’ (or water-attracting) and assist in rendering the detergents soluble in water.

(ii) *Non-ionic detergents*—These do not ionize at all in aqueous solution. A well-known example is Lissapol N, a condensation product of ethylene oxide and an alkylated phenol.

(iii) *Cationic detergents*—These are salts of strong quaternary organic bases and ionize in aqueous solution giving a positively charged hydrophobic quaternary ammonium or pyridinium group (cation) and a negatively charged hydrophilic group (anion). They have strong bactericidal properties and are therefore used for washing utensils in hotels and restaurants. They are at present too expensive for general use and the small amounts finding their way into sewage would probably be precipitated by the anionic detergents normally present.

Examples of all three groups of synthetic detergents are given in Table 9.

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
<th>Typical structure</th>
<th>Tendency to cause foam</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anionic</td>
<td>Sodium alkyl sulphate</td>
<td>R−[SO₂Na]</td>
<td>Much</td>
</tr>
<tr>
<td></td>
<td>Sodium alkyl aryl sulphonate</td>
<td>R·C₆H₄−SO₃Na</td>
<td>Much</td>
</tr>
<tr>
<td>Non-ionic</td>
<td>Polyglycol ether of alkylated phenol</td>
<td>R·C₆H₄−(C₂H₄O)ₙ−OH</td>
<td>Little*</td>
</tr>
<tr>
<td></td>
<td>Quaternary ammonium compounds</td>
<td>R+(CH₃)₂N−CI</td>
<td>Much</td>
</tr>
<tr>
<td>Cationic</td>
<td>Cetyl pyridinium bromide</td>
<td>C₂₀H₴₀−N−Br</td>
<td>Much</td>
</tr>
</tbody>
</table>

(R, R', R", represent long chain hydrocarbon radicles.)

The types of synthetic detergent found in sewage and rivers are mostly the *anionic types* but the *non-ionic types* are increasing in...
ASPECTS OFIVER POLLUTION

... popularity and it is reported that together these two types represent 90 per cent of the synthetic detergents used in the U.S.A.

The increasing use of synthetic detergents in place of soap is causing considerable concern to sewage works authorities, river boards, and water undertakings on account of the masses of foam caused by the presence of even low concentrations of these detergents. Aeration (e.g. passage of a river over a weir) tends to increase the amount of foam. The production of foam is a physical phenomenon due to the lowering of the surface tension of water and sewage by the detergents. At activated sludge aeration plants of all types, but especially at diffused air plants, the foam is particularly troublesome and becomes airborne in windy weather. Many methods have been proposed for the control of foam at activated sludge plants. These include maintaining the suspended solids in the mixed liquor at a high level, spraying the surface of the tanks with about 0.1 p.p.m. of mineral oil, spraying the aeration tanks with plant effluent, and the use of various proprietary anti-foam chemicals, but it cannot be said that any of these methods offers a general solution to the problem.

Whilst there is no established proof that synthetic detergents are definitely responsible for the present-day foaming troubles, nevertheless it is significant that whenever a manufacturer distributes free samples of synthetic detergent preparations to a particular district or town, the inevitable result is a big increase in foaming at the local sewage works and in the river receiving the sewage works effluent. The foam is sometimes so high (often several feet) and so light that it can create a nuisance through being blown about by the wind, and has sometimes even been mistaken for 'flying saucers'. At certain sewage disposal works there is much evidence of greater difficulty in treating sewage containing detergents, and in the woollen districts of Yorkshire in the recovery of the valuable wool grease from the sewage. The work of HURLEY has shown that Teepol (a sodium higher alkyl sulphate) does not materially affect the oxidation of sewage and, being almost completely removed from sewage by biological filtration, does not normally cause foaming in streams. On the other hand, LUMBER has proved that small concentrations (20 p.p.m. in the crude sewage) of detergents of the alkyl aryl sulphonate class (one of the most commonly used types) as well as non-ionic detergents do, in fact, adversely influence the oxidation of sewage in percolating filters and by activated sludge; they are incompletely oxidised biologically and so the final effluents contain enough detergents to give rise to persistent foam on agitation. Similar differences in the ease of biological oxidation of alkyl sulphates and alkyl aryl sulphonates have been observed by DEGGS and his co-workers.
at Amsterdam, Holland. Recent studies by Bogan and Sawyer in the U.S.A. on the biochemical oxidation by activated sludge of synthetic detergents in sewage has confirmed and extended much of the earlier work. They showed that whilst certain detergents (e.g. alkyl sulphates and sulphonated fatty esters and amides) are easily oxidized biochemically, others (e.g. alkyl aryl sulphonates and alkyl phenoxy polyglycols) are relatively resistant to biochemical oxidation. Unfortunately, the latter types which resist oxidation and so largely pass unchanged through a sewage plant and thence to streams are being used in ever increasing quantities.

According to Isaac, the average concentration of synthetic detergents in sewage in the United Kingdom, estimated on the basis of their average consumption, was 14-15 p.p.m. in 1952. Since the most commonly used synthetic detergents in this country (the alkyl aryl sulphonates) are only removed from sewage even under favourable conditions to the extent of about 50-60 per cent by biological processes, it is evident that approximately one-half (or about 7 p.p.m.) of the detergent passing to the sewage works will eventually find its way to the river. If the dilution afforded by the river is adequate, probably little harm will result, but at times of low flow or on streams where there is little dilution by clean water and the stream consists mainly of sewage effluents the position might become serious especially where water supplies are drawn from the river. On the River Lee, for example, considerable foaming has been reported about 12 miles above one of the water intakes of the Metropolitan Water Board. It is, therefore, natural that this board should be very seriously concerned about the position, for who would contemplate with equanimity the prospect of a housewife turning on her water tap only to find masses of foam emerging? Lumsden foresees a big increase in the concentration of synthetic detergents in the sewages of the future, and possibly, therefore, in our rivers, and he suggests that the consumption of synthetic detergents may reach about 9 lb. per capita per annum in many areas favourable to their use and so may produce a concentration of as much as 70-100 p.p.m. in some sewages. The problems raised are therefore likely to become more acute as time goes on.

There have been reports from the U.S.A. about operating troubles due to synthetic detergents at some waterworks drawing their supplies from rivers at times of low flow. For instance, Culp and Stoltenberg have reported the formation of large amounts of foam at the waterworks at Osawatomie, Kansas, taking its supplies from the Marais des Cygnes river. The cause of the trouble was traced to the presence of synthetic detergents in the effluent from a sewage works, the minimum concentration of detergents producing interference being 3-0-3-5 p.p.m.
Some synthetic detergents persist for a long time in streams. Aquarium tank experiments on the biological decomposition of detergents in water, carried out by Degens and his co-workers, have shown that alkyl sulphonates (e.g. Teepol) are readily oxidized biologically whereas an alkyl aryl sulphonate and a non-ionic detergent (polyglycol ether of an alkylated phenol) were only slowly oxidized under similar conditions. These results find a parallel in the previously mentioned work of Hurley and Lumb (page 44) on the oxidation of synthetic detergents in sewage. It seems probable, therefore, that detergents of the alkyl aryl sulphonate type and of the non-ionic type are likely to persist for long periods in rivers and to cause foaming troubles, and perhaps also adverse effects on fish and vegetation (cf. page 26) for long distances.

Interesting work has recently been described by Hammerton on the relationship between the chemical structure of anionic synthetic detergents and their susceptibility to oxidation by bacterial action in river water. His experiments suggest that the reason for the easy breakdown of some detergents and the relative resistance of others lies not necessarily in the presence of sulphate or sulphonate groups but rather in the structure of the alkyl group present in the molecule. Detergents such as Teepol or Drene, containing a straight-chain alkyl group (e.g. CH\(\text{CH}_2\)\(_n\)), are easily oxidized biochemically in a few days whereas those containing a branched-chain alkyl group, e.g.

\[
\text{CH}_3\text{CH}-(\text{CH}_2)_n-\text{CH}_3
\]

exhibit very much more resistance to oxidation, the most resistant being those with the most highly branched chain. Thus, the compound Tergitol 7 (the sodium salt of a secondary alkyl sulphate), with the following structure,

\[
\begin{align*}
\text{C}_2\text{H}_5\text{CH}-(\text{CH}_2)_2\text{CH}(\text{CH}_2)\text{CH}-(\text{CH}_2)_2\text{C}_2\text{H}_3 \\
\text{C}_2\text{H}_5 \quad \text{OSO}_3\text{Na} \quad \text{C}_2\text{H}_5
\end{align*}
\]

is, although a sulphate, very resistant to biochemical oxidation because of the presence of a much-branched chain.

According to Roberts, 1 p.p.m. or even less of synthetic detergent can cause frothing on rivers especially where the river flows over a weir, and the persistence of the foam appears to be associated with a high atmospheric humidity (70 per cent of saturation or over) and low wind. Foam is particularly troublesome on the River Lee in the neighbourhood of Luton but methods for destroying this foam have not succeeded in producing lasting effects down the river.
many rivers, apart from the aesthetic objection to froth, there does not seem to be any evidence of any marked harmful effects. Nevertheless, froth at a sewage works does collect a certain amount of oil and grease which may possibly harbour pathogenic organisms. Donaldson states that foam from the final effluent of an activated sludge plant in the U.S.A. contained 30–50 per cent of greasy matter (based on the total solids).

The importance of the synthetic detergent problem in this country is such that the Ministry of Housing and Local Government has appointed a committee of experts to examine and report on the effects of the growing use of these detergents and to make any recommendations which seem desirable, special reference being given to the functioning of the public health services. This committee has now presented an Interim Report from which it appears that the most serious problems are in connection with the treatment of sewage. Some concern was felt also for the condition of our rivers and the purity of our water supplies. They reported that at many activated sludge plants, foam several feet high is often produced during the aeration of the 'mixed liquor'. The drifting of this foam, say the committee, makes it offensive to the neighbourhood. Consequently in the interests of public health, the suppression of the foam is of vital importance, but further research is needed before a simple and cheap method of control could be recommended.*

**Radioactivity**

Most elements can now be obtained in different varieties called 'isotopes', having the same nuclear charge but different mass numbers, and some of these are radioactive. An element is said to show radioactivity when it is unstable and disintegrates spontaneously with the emission of one or more types of radiation.

Although the phenomenon of radioactivity has been known for over fifty years, it must be remembered that many radioactive elements have always existed on the earth. Most natural waters have slight radioactivity usually not exceeding $10^{-3}$ μ-curie/l.

A curie is defined as the quantity of radioactive substance which disintegrates at a rate of $3.7 \times 10^{10}$ disintegrations per second and is the number of disintegrations which occur in 1 g of radium. Hence, a micro-curie is a millionth part of this, that is $3.7 \times 10^4$ disintegrations per second.

The potassium present in vegetables, in food, and in our bodies contains a minute proportion of a radioactive isotope. Atmospheric

* A Final Report of this committee (June, 1956) has now been published.
carbon dioxide contains a very small amount of a radioactive isotope of carbon.

It was, however, during the period following World War II that the truly amazing development of nuclear fusion processes took place at atomic energy establishments, resulting in the production of large volumes of highly radioactive waste waters. The safe and convenient disposal of these wastes without danger to public health or to life in rivers has created a new and difficult problem which is likely to become more acute as development of atomic energy progresses. In addition, the use of artificially produced radioactive isotopes for research and other purposes both in hospitals and in industry is likely to increase. For example, a radioactive isotope of iodine (iodine-131) is now extensively used for medical purposes and may therefore be present in sewage. Belcher states that iodine-131 is not appreciably removed by normal sewage treatment processes (biological filtration or activated sludge), hence it may find its way to a river and be a potential source of danger to domestic water supplies drawn from the river. It has, however, been shown that traces of silver nitrate (0.085 p.p.m., expressed as silver) added to such waters before coagulation give more than a 90 per cent removal of iodine-131.

It can be said, then, that radioactivity has somewhat suddenly come to the fore as a potentially dangerous form of river pollution. Fortunately methods for dealing with this menace have been developed.

The disintegration of radioactive elements involves the release of many different types of radiation highly damaging in varying degrees to animals, plant life, and man. The most important of these are alpha-, beta- and gamma-rays.

Alpha-rays are relatively large particles highly damaging to tissues and bone and having intense ionizing powers. They consist of helium nuclei of mass 4 with two positive charges. Although very harmful, they are not very penetrating and they can easily be shielded by a thin sheet of metal.

Beta-rays are negatively charged particles (electrons) of a moderately damaging character and with moderate penetrating powers (they can penetrate thin metal sheets) but with smaller ionizing powers than the alpha-rays.

Gamma-rays are highly penetrating radiations similar to the well-known X-rays. They are rather less damaging than are alpha- and beta-radiations, but owing to their much greater penetrating powers (they can penetrate several centimetres of lead) they require much more thorough and extensive shielding.

The energies of these various radiations are characteristic of a particular radioactive isotope but vary from one radio-element to
another, making some of the elements very dangerous and others relatively harmless. In working with materials emitting these rays, some form of shielding from the penetrating and injurious radiations is essential. Bacteria appear to be far more resistant to all these radiations than are human beings.

Radioactive elements in whatever physical state or state of chemical combination disintegrate at a rate which is characteristic for the particular isotope and which cannot be influenced by any known means. The activity of a radioactive element falls off exponentially according to the equation

\[ N_t = N_0 e^{-\lambda t} \]

where \( N_0 \) = number of atoms present at the beginning

\( N_t \) = number of atoms present after \( t \) seconds

\( e \) = base of natural logarithms (\( = 2.71828 \ldots \))

and \( \lambda \) = a constant called the disintegration constant

An important characteristic of each radio-element is its 'half-life', or the time taken for \( \frac{1}{2} \) of the atoms to disintegrate. The half-life, \( t_h \), can be found by substituting \( \frac{N}{2} \) = \( \frac{1}{2} \) in the above exponential equation, when we get

\[ \frac{1}{2} = e^{-\lambda t_h} \]

therefore

\[ \lambda t_h = - \log_e \frac{1}{2} = -(1.307) = -(-0.693) \]

or

\[ t_h = \frac{\log_e 2}{\lambda} \]

The half-life can vary from a fraction of a second for very unstable isotopes to thousands of millions of years for the very stable radio-elements. Table 10 gives the half-life periods of some of the better-known radioactive elements, together with their mass numbers and the type of radiation emitted.

After the half-life period has elapsed, a radio-element will have disintegrated so that \( \frac{1}{2} \) of the atoms have broken down and \( \frac{1}{2} \) remain unchanged. After twice the half-life period, it is evident that \( \frac{1}{2} + \frac{1}{2} = \frac{3}{2} \) of the atoms will have decayed whilst \( \frac{1}{2} \) will remain. Table 11 shows this process carried up to \( 10 \times t_h \).

It will be seen from this table that after a period of time ten times the half-life, only \( \frac{1}{1024} \) or less than 0·1 per cent of the original element remains. It follows that provided the half-life period of a radio-element is reasonably short (which is the case with the
elements in the upper part of Table 10), storage can be a very effective method of reducing the radioactivity.

Table 10. Half-life periods of some radioactive elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Mass No. of isotope</th>
<th>Half-life</th>
<th>Radiation emitted</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium</td>
<td>24</td>
<td>14.9 hours</td>
<td>β, γ</td>
</tr>
<tr>
<td>Potassium</td>
<td>42</td>
<td>12.4 hours</td>
<td>β</td>
</tr>
<tr>
<td>Bromine</td>
<td>82</td>
<td>36 hours</td>
<td>β, γ</td>
</tr>
<tr>
<td>Iodine</td>
<td>131</td>
<td>8 days</td>
<td>β, γ</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>32</td>
<td>14.3 days</td>
<td>β</td>
</tr>
<tr>
<td>Strontium</td>
<td>89</td>
<td>53 days</td>
<td>β</td>
</tr>
<tr>
<td>Cobalt</td>
<td>60</td>
<td>5.3 years</td>
<td>β, γ</td>
</tr>
<tr>
<td>Radium</td>
<td>226</td>
<td>1,500 years</td>
<td>α, β, γ</td>
</tr>
<tr>
<td>Carbon</td>
<td>14</td>
<td>5,700 years</td>
<td>β</td>
</tr>
<tr>
<td>Plutonium</td>
<td>239</td>
<td>24,100 years</td>
<td>s</td>
</tr>
<tr>
<td>Uranium</td>
<td>238</td>
<td>4,510,000,000 years</td>
<td>s</td>
</tr>
</tbody>
</table>

Table 11. Disintegration of radio-elements after various multiples of the half-life period, $t_i$

<table>
<thead>
<tr>
<th>After time $n t_i$</th>
<th>Fraction of No. of atoms disintegrated</th>
<th>Fraction of No. of atoms remaining</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 t_i</td>
<td>1/2</td>
<td>1/2</td>
</tr>
<tr>
<td>3 t_i</td>
<td>3/4</td>
<td>1/4</td>
</tr>
<tr>
<td>4 t_i</td>
<td>7/8</td>
<td>1/8</td>
</tr>
<tr>
<td>5 t_i</td>
<td>15/16</td>
<td>1/16</td>
</tr>
<tr>
<td>6 t_i</td>
<td>31/32</td>
<td>1/32</td>
</tr>
<tr>
<td>7 t_i</td>
<td>63/64</td>
<td>1/64</td>
</tr>
<tr>
<td>8 t_i</td>
<td>127/128</td>
<td>1/128</td>
</tr>
<tr>
<td>9 t_i</td>
<td>255/256</td>
<td>1/256</td>
</tr>
<tr>
<td>10 t_i</td>
<td>511/512</td>
<td>1/512</td>
</tr>
</tbody>
</table>

The experimental techniques for the detection and measurement of radioactivity are still changing fairly rapidly and must be used in laboratories specially equipped for the purpose with expensive instruments for carrying out measurements and with safety devices for protecting personnel from the harmful radiations. Although these instruments enable us to count the number of disintegrations, only a complicated radiochemical analysis will indicate whether the activity arises from a dangerous element. It would be impracticable for such work to be carried out at the present time in the ordinary chemical laboratories of a sewage works or river board.

The Ministry of Housing and Local Government now has on its staff a radiochemical inspector with expert knowledge of radiochemistry who is able to give advice on all problems involving the
disposal of radioactive wastes. According to Key and Kenny,71 the Medical Research Council Protection Committee has approved the following lifetime drinking-water tolerance concentrations which are considered safe to add to the River Thames so as to avoid long-period accumulation of radioactivity:

**Alpha-emitters**
- Radium: $4 \times 10^{-10}$ μ-curies/ml.
- Other α-emitters: $2.4 \times 10^{-9}$ μ-curies/ml.

**Beta-emitters**
- Radio-calcium and Strontium: $2 \times 10^{-8}$ μ-curies/ml.
- Other β-emitters: $10^{-6}$ μ-curies/ml.

Key and Kenny stress the fact that these figures are unbelievably minute. For instance, in the case of radium, the concentration works out at only $4 \times 10^{-10}$ p.p.m. whilst in the case of radio-calcium it is a mere $1.2 \times 10^{-12}$ p.p.m.

Section 5 of the Radioactive Substances Act, 1948, enables a Minister to make regulations for the purpose of securing a safe disposal of waste radioactive substances, and any breach of the regulations is an offence. At present, however, there is no real necessity for regulations, for as Key and Kenny point out, a record is kept of all radioactive materials sent out from Harwell and other similar establishments and of their destinations and so it is possible to calculate the relationship between the activity and the volume of sewage in a particular district. So long as the sewage of the district is not contaminated up to the lifetime tolerance levels already quoted for drinking-water, there cannot be any danger to public health. As a safeguard to the community, under the recent Atomic Energy Authority Act, 1954, authorization to dispose of or discharge radioactive wastes shall not be given until the Ministers of Housing and Local Government and of Agriculture, Fisheries and Food have consulted river boards and other public and local authorities concerned. Nevertheless, there is already apprehension amongst those concerned with public health, water supplies, etc., and amongst all who are interested in underground exploration (speleologists) about the proposed use of abandoned mines for the disposal of radioactive wastes. There is always the possibility that such practices might lead to contamination of water supplies or to pollution of streams.

**Physiological Types of Pollution**

In view of the steadily rising consumption of water in this country and the difficulty of finding additional underground and upland...
sources, increasing use is likely to be made in the future of rivers as sources of supply. If shortage of available supplies makes it necessary to use the more polluted reaches of rivers for potable water supplies, the problem of taste may well assume considerable importance. Industrial wastes contain many chemical compounds which impart characteristic and unpleasant tastes to water; for instance, salts, iron, manganese, free chlorine, hydrogen sulphide, phenols and unsaturated hydrocarbons. Many of these substances can be removed fairly easily by conventional water purification processes (see page 96) but this is not always the case. Thus, Besozzi and Vaughan72 have reported that it was practically impossible to produce economically a drinkable water free from taste and odour at Whiting, on the shores of Lake Michigan, since the lake from which the town takes its supplies receives considerable pollution from oil refinery wastes. Again, it has been reported73 that during the winter of 1948-9, there were complaints of a mouldy or mildewy taste in the water supply of Appleton, Wisconsin, U.S.A., which could not be removed by activated carbon. This unpleasant taste was attributed to the presence of synthetic detergents derived from sewage effluents in the sources of supply (Fox river and Lake Winnebago). When the water was treated with chlorine dioxide, however, complaints of the taste ceased.

Extremely minute quantities of certain substances can impart a taste to water. The 'inky' taste of ferrous iron can be detected74 at a dilution of 1 in 10,000,000 (i.e. 0·1 p.p.m.), but ferric iron can only be tasted74 at a dilution of 1 in 5,000,000 (i.e. 0·2 p.p.m.). Tastes due to free chlorine may be evident when as little as 1 part of chlorine is present in 10,000,000 parts of water (i.e. 0·1 p.p.m.). Southgate75 states that phenol produces a taste when present in water to the extent of 7 p.p.m. When water containing phenol is chlorinated, as little as 0·002 p.p.m. of phenol can cause a perceptible taste75 due to the formation of chlorophenols which have an intense taste and odour. Danol and Nietsch76 claim that the taste of only 0·001 μg of a petroleum oil in a litre of well water (i.e. only 0·000001 p.p.m.) is clearly perceptible after 2-3 minutes.

River waters polluted by trade wastes often contain taste-producing substances (e.g. phenols, chlorophenols) which may damage the value of fisheries by imparting unpleasant tastes to fish. Banov77 in a review of this subject states that synthetic rubber waste waters contain taste-producing hydrocarbons (e.g. styrene) and aldehydes; explosives factory waste waters contain traces of nitro derivatives of benzene and toluene which impart a 'bitter almond' flavour to fish; and oil refinery wastes give an objectionable taste to fish on account of the presence of naphthenic acids. Many of these tastes can be removed by keeping the fish for some time in
pure water. Experiments by BoETUS on the carbolic taste acquired by eels, trout, herring, and oysters in a fjord polluted by waste waters from a factory manufacturing weed killers and insecticides, showed that the taste was due mainly to chlorophenol.

Peculiar tastes can be imparted to water by the decomposition of organic matter, and of algae, fungi, and filamentous bacteria.

ODOUR

The layman has no doubts about the polluted condition of a river if it 'smells', hence the odour of a river is often one of its most important characteristics. Odour may be caused by the presence of certain strong-smelling chemical compounds (e.g. ammonia, phenols, free chlorine, sulphides, cyanides) which can easily be identified and estimated, or it may be associated with many organic materials (e.g. essential oils), with algae and other vegetable organisms, and with decomposing and putrescent organic matter. Many kinds of odour (e.g. grassy, earthy, musty, mouldy, vegetable) may be caused by minute traces of substances which cannot easily be identified by chemical analysis. Certain micro-organisms have been shown to be responsible for odours in water supplies. For example, the protozoa Dinobryon and Uroglena and the alga Volvox impart a fishy smell to water; the algae Oscillatoria and Rivularia, a mouldy odour; and the alga Anabatna, a strong grassy odour. Fair and Whipple have suggested that these odours may be caused by the liberation of traces of essential oils.

Most unpleasant smells associated with polluted rivers are due to the presence of inorganic and organic compounds of nitrogen, sulphur, and phosphorus and arise from the putrefaction of proteins and other organic materials present in sewage and in trade wastes. Some of the very worst smells are caused by compounds of sulphur, such as hydrogen sulphide (H₂S) and the mercaptans (R·SH, where R = a hydrocarbon radicle). The Royal Commission on Sewage Disposal classified smells arising from polluted rivers as follows:

(a) Putrid smell (due mainly to H₂S).
(b) Fishy smell (due probably to organic amines).
(c) Wormy smell (due possibly to phosphorus compounds).
(d) Earthy smell (due to humus).

It was stated that the 'stale water' smell near rivers is generally neither strong nor objectionable and is due to the effect of (c) and (d). On the other hand, odours due to (a) and (b) may be very strong and may occur not only when the river water becomes completely deoxygenated but also even in the presence of
some dissolved oxygen if putrefying mud is present on the river bed.

Undoubtedly, the commonest cause of complaints of objectionable smells arising from streams is the presence of small amounts of sulphides. The extent of this odour nuisance appears to depend mainly on the pH value of the river water and on the concentration of dissolved sulphide present in the water. The lower the pH value, the greater is the amount of 'free' \( \text{H}_2\text{S} \) liberated, and the higher is the degree of atmospheric pollution which results.

It is remarkable how a very minute concentration of certain compounds can be detected by odour. In order to illustrate this, Table 12, compiled from data in the literature\(^77\), shows the odour thresholds of a few substances found in sewage and trade wastes.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Formula</th>
<th>Approximate concentration having just noticed (ppm)</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>( \text{NH}_3 )</td>
<td>0·037</td>
<td>pungent, 'ammoniacal', alkaline</td>
</tr>
<tr>
<td>Amyl acetate (iso)</td>
<td>( \text{CH}_3\text{COOC}_6\text{H}_5(\text{CH}_3)_2 )</td>
<td>0·0006</td>
<td>pear drops</td>
</tr>
<tr>
<td>Benzenethiol</td>
<td>( \text{C}_6\text{H}_5\text{CHO} )</td>
<td>0·003</td>
<td>bitter almonds</td>
</tr>
<tr>
<td>Carbon disulphide</td>
<td>( \text{CS}_2 )</td>
<td>0·0026</td>
<td>very unpleasant, nauseating</td>
</tr>
<tr>
<td>Chlorine</td>
<td>( \text{Cl}_2 )</td>
<td>0·010</td>
<td>chlurous</td>
</tr>
<tr>
<td>Chlorophenol</td>
<td>( \text{C}_6\text{H}_4\text{H}_2\text{OH} )</td>
<td>0·00018</td>
<td>TCP, 'medicinal'</td>
</tr>
<tr>
<td>Ethyl mercaptan</td>
<td>( \text{CH}_3\text{CH}_2\text{SH} )</td>
<td>0·0019</td>
<td>putrid green vegetables</td>
</tr>
<tr>
<td>Hydrogen cyanide</td>
<td>( \text{HGN} )</td>
<td>0·001</td>
<td>bitter almonds</td>
</tr>
<tr>
<td>Hydrogen sulphide</td>
<td>( \text{H}_2\text{S} )</td>
<td>0·0011</td>
<td>bad eggs</td>
</tr>
<tr>
<td>Methyl mercaptan</td>
<td>( \text{CH}_3\text{SH} )</td>
<td>0·0011</td>
<td>putrid green vegetables</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>( \text{C}_6\text{H}_4\text{NO}_2 )</td>
<td>0·03</td>
<td>bitter almonds</td>
</tr>
<tr>
<td>Skatole</td>
<td>( \text{C}_9\text{H}_9\text{N} )</td>
<td>0·0012</td>
<td>faecal, nauseating</td>
</tr>
<tr>
<td>Sulphur dioxide</td>
<td>( \text{SO}_2 )</td>
<td>0·009</td>
<td>pungent, acid</td>
</tr>
</tbody>
</table>

There is a considerable variation amongst individuals in their ability to smell. For example, many persons find considerable difficulty in detecting the bitter almond odour of hydrogen cyanide (prussic acid) and cyanides in trade wastes and polluted waters. In this connection, it is interesting to note that the ability to smell HCN is now thought to be an inherited characteristic involving a sex-linked recessive gene\(^80\),\(^81\) and this may also be true of the ability to smell other substances.

Many complaints of pollution of watercourses are associated with 'smells'. It is important, however, to sound a note of warning
NATURE AND EFFECTS OF POLLUTION

Nuisance due to bad smells arising from a polluted stream must be carefully distinguished from atmospheric pollution in the vicinity of the stream caused by smells from a particular industrial process, which are more properly the concern of the local sanitary inspector rather than the river board. Moreover, objectionable odours, however unpleasant, are not in themselves known to be injurious to public health unless they arise from certain toxic chemical gases and vapours.

The elimination of odours in drinking-water can often be accomplished by use of a few p.p.m. of activated carbon, which has the additional advantage of removing tastes. Other useful methods involve the use of chlorine, chlorine dioxide, ozone, and aeration (cf. page 97). Chlorination is sometimes a useful method for controlling odours of industrial wastes.

The value of nitrates in polluted streams for preventing bad smells is now well recognized. JAPSON and GREENE82 conclude from their experiments that provided a stream is reasonably pure the nitrate content is of little value so long as dissolved oxygen is present, but if the stream is heavily polluted and is denuded of dissolved oxygen, then the combined oxygen supplied by nitrates can be of very great importance. Apparently, the oxygen supplied by nitrates is not utilized by bacteria until all free dissolved oxygen has disappeared and so the nitrates act as a kind of last line of defence in preventing anaerobic conditions and foul odours in a river. In the U.S.A. there are several reports of the deliberate addition of nitrates to polluted streams in order to prevent or eliminate odour nuisance. Thus, LAWRENCE85 states that sodium nitrate was used successfully to stop bad smells due to hydrogen sulphide in the Androscoggin river which was polluted by sulphite waste liquors from paper mills; it is interesting to note that this procedure did not stimulate growth of blue-green algae, although no less than 641.5 tons of sodium nitrate were added during 44 days in the summer of 1949. TODD84 reports the case of a stagnant creek (B.O.D. = 35 p.p.m.) containing sewage which caused complaints of foul odours during a period of drought; sodium nitrate (72 p.p.m.) was added when the smell disappeared after 7 hours and did not reappear for 7 days. Pollution of the San Antonio river by brewery wastes caused unpleasant odours at a time when the river flow was low during a drought; the smells were successfully controlled by the addition of 150 lb. of granular sodium nitrate over 4 days (a solution of sodium nitrate gave unsatisfactory results). Pea canning wastes are often treated in lagoons in the U.S.A. and during hot weather this results in very foul odours which, according to RYAN86, can be controlled by adding sodium nitrate.

In connection with the stabilization by nitrates of waters polluted
by sewage and other organic wastes, Buswell suggests that the reactions occurring can be represented by one of the following equations:

\[ \text{C + 2NaNO}_3 = \text{Na}_2\text{CO}_3 + \text{N}_2 \quad \text{(Nitrogen production)} \]

\[ 2\text{C} + \text{NaNO}_3 + 3\text{H}_2\text{O} = \text{NaHCO}_3 + \text{NH}_4\text{HCO}_3 \quad \text{(NH}_3 \text{ formation)} \]

Stones has pointed out that the course of decomposition of nitrates can occur in the following possible ways:

1. \[ \text{HNO}_3 + \text{H}_2\text{O} = \text{NH}_3 + 4\text{O} \quad \text{(NH}_3 \text{ formation)} \]
2. \[ 2\text{HNO}_3 = \text{N}_2 + \text{H}_2\text{O} + 5\text{O} \quad \text{(Nitrogen production)} \]
3. \[ \text{HNO}_3 = \text{HNO}_2 + \text{O} \quad \text{(Nitrite formation, followed by reaction with ammonia to give nitrogen)} \]

He incubated settled filter effluent and settled sewage containing nitrate for 5 days at 65° F and 80° F and showed that although large quantities of nitrate disappeared there was no corresponding increase in the amount of ammonia, thus suggesting that nitrates are reduced to nitrogen rather than to ammonia.

**BIOLOGICAL KINDS OF POLLUTION**

Under this heading, we must include pathogenic bacteria, certain fungi, algae, viruses, pathogenic protozoa, parasitic worms, and, indeed, any plants or animals which for some reason either multiply excessively in a stream or are otherwise undesirable, harmful or injurious.

Biological pollution is often a secondary result of pollution by sewage. The excessive growth of certain green sea-weeds in Belfast Lough was investigated by the Royal Commission on Sewage Disposal. These plants underwent decomposition with evolution of sulphuretted hydrogen, thus causing much nuisance. The presence of Belfast sewage was found to favour the growth of these weeds so among the remedial measures suggested was the settlement of the sewage before discharge. Lieber has reported that excessive growths of the annual freshwater plant water chestnut (Trapa natans) in streams in the U.S.A. are due to the discharge of untreated sewage or effluents, thus causing fish mortality and bad smells during the summer, and, in addition, serving as breeding grounds for mosquitoes. The best method of dealing with this menace was to cut the plants by machine in May or June before they reached maturity. Excessive growths of "sewage fungus" (page 60) are also a secondary result of the discharge of sewage or trade effluents.
Biological pollution is probably the explanation of the following curious passage in the Old Testament:

'Behold, I will smite with the rod that is in mine hand upon the waters which are in the river, and they shall be turned to blood. And, the fish that is in the river shall die, and the river shall stink; and the Egyptians shall loathe to drink of the water of the river.' Exod. vii. 17, 18.

The red colour mentioned in this passage may have been caused by the growth of red or brown algae, or perhaps by the growth of purple sulphur bacteria (page 139). Excessive growths of algae often suddenly appear in reservoirs, causing odours in the water and considerable nuisance when the plants die and undergo decomposition (page 83). Olson90 states that certain blue-green algae are toxic to human beings and animals, and can cause epidemics of gastro-enteritis.

Many of the common infections of man (e.g. influenza, smallpox, poliomyelitis and yellow fever) are virus diseases and consequently the possibility of virus contamination of our rivers must not be overlooked. Viruses are the smallest living micro-organisms and are capable of growth only within the living cells of a susceptible host91. Viruses differ from bacteria not only in their much smaller size but also in their inability to grow in artificial media and in their much greater resistance towards disinfectants. One of the most important and dreaded of virus diseases is poliomyelitis (formerly called infantile paralysis) which may cause paralysis of one or more parts of the body due to the destruction by the virus of a certain number of nerve cells controlling the muscles. The disease occurs all over the world and according to Landworthv92 reached a new high record in 1952 in the U.S.A. Poliomyelitis virus has been detected in the stools of patients suffering from the disease and in the stools of healthy carriers as well as in sewage during an epidemic of the disease93.94. Experiments carried out in South Africa95 have demonstrated the presence of the virus in raw sewage sludge, settled sewage, septic tank effluent, and in humus tank effluents, but not in sewage sludge digested for 30 days or in a sand filter effluent. Thus, humus tank effluent could contaminate streams with the virus and if used for irrigation might contaminate vegetables or fruit. On the other hand, filtration of a sewage effluent through sand apparently removes the virus. Activated sludge appears to remove most of the virus from sewage and the presence of an anti-viral substance in activated sludge has actually been demonstrated96.97. Small quantities of chlorine88, or better still treatment with chlorine
dioxide, can be used to destroy the virus in water but sewage would probably require fairly large amounts of disinfectant. Work on the survival of poliomyelitis virus in experimentally infected river water has shown that the virus can survive in river water for quite long periods (up to 6–7 months). Nevertheless, there is at present insufficient evidence to justify the hypothesis that poliomyelitis is a water-borne disease for there are many other possible ways in which it might be spread, e.g. by animals, flies and contaminated milk.

The most widespread form of biological pollution, namely contamination of watercourses by pathogenic bacteria derived from sewage, is discussed in the following section. It is unusual for trade wastes to contain pathogenic bacteria but tannery wastes may contain the very resistant spores of anthrax bacilli derived from the hides.

SEWAGE AND ITS COMPOSITION

Sewage is a cloudy very dilute aqueous solution containing inorganic and organic matter partly in true solution, partly in colloidal solution, and partly in suspension. Soapy wastes from houses, urine, and faeces are present, and there may also be paper, garbage, rags, matchsticks, oil, etc., floating on the surface. In wet weather, street and roof washings make a significant contribution to the total. The amount of these washings will depend not only on the intensity of the rainfall but also upon the type of sewerage system; the system may be ‘combined’ (i.e. all drainage going to the sewage works), ‘separate’ (i.e. one set of sewers for foul water going to the sewage works and a second set for surface water going direct to the river), or ‘partially separate’ (a compromise between the other two systems). Some ground water (‘infiltration water’) also leaks into nearly all sewerage systems as sewers rarely have water-tight joints. The composition, character, and appearance of sewage may also be profoundly modified by the presence of trade wastes. For example, sewage containing gas liquor is more difficult to purify than domestic sewage, and it has a pale reddish-brown colour instead of the greyish colour of ordinary domestic sewage. The water content of sewage may be as much as 99.9 per cent or more so that the total dry solid matter (organic and inorganic) is only 0.1 per cent or less. Southgate states that settled domestic sewage contains about 250–400 p.p.m. of organic carbon and about 80–120 p.p.m. of total nitrogen, thus giving a C:N ratio of about 3. Industrial sewages may contain much more organic matter and so may have a higher C:N ratio. The nitrogen in sewage is present partly as organically bound nitrogen and partly as ammoniacal
nitrogen (i.e. "free and saline ammonia"); the latter constitutes about 50-75 per cent of the total nitrogen. Urine contains about 1 per cent of sodium chloride (NaCl) and about 2-5 per cent of urea (NH₂·CO·NH₂) as well as complicated organic substances. The sodium chloride in sewage is derived partly from urine, in part from the water supply and partly from salt present in trade wastes. Other inorganic constituents of sewage, such as calcium sulphate, sodium sulphate, sodium and calcium bicarbonates, sodium phosphate, etc., are derived chiefly from the water supply but many salts, of course, originate from trade wastes present in sewage.

Faeces and household wastes supply sewage suspended matter as well as matter in colloidal and true solution in the form of fats, soaps, proteins, carbohydrates and their decomposition products. Sewage may vary considerably in composition and strength from town to town and from country to country owing to marked differences in the habits of the population, the nature of the diet, the composition of the trade wastes present, and the water consumption.

Southgate, from an analysis of data issued by the former Ministry of Health, states that at 112 representative sewage works in Great Britain the average volume of sewage treated daily in dry weather varies from 10-100 gallons per head of population served, with an average of 37 gallons per head. These figures are based on pre-war data and may be expected to be somewhat greater today. The higher water consumption in the U.S.A. leads as a rule to much greater sewage flows than are experienced in this country and figures of well over 100 gallons per capita per day are by no means unusual in American cities.

Bacteria are present in sewage and farm drainage in very large numbers (several millions per ml.). Bacteria, of course, abound everywhere on the earth’s surface, even in natural unpolluted waters, but sewage with its varied content of easily decomposable organic matter is an excellent medium for the development of bacteria. Most sewage bacteria are relatively harmless and belong to the class of "saprophytic" bacteria (i.e. bacteria which only feed upon dead organic matter). A few bacteria are, however, dangerous since they belong to the class of "pathogenic" bacteria (i.e. bacteria which cause disease in man and animals) and are, therefore, important from a public health standpoint; these are not normally present in large numbers in sewage in this country except during epidemics. Among the most important of the pathogenic bacteria liable to cause infection in this country are B. typhosa* (causing typhoid fever), B. paratyphi† (causing paratyphoid fever), B.

* Now usually called Salmonella typhi.
† Now usually called Salmonella paratyphi.
dysenteriae* (causing bacillary dysentery), *Vibrio cholerae* (causing cholera, but now very rare in this country), and many bacteria of the *Salmonella* group (causing gastro-enteritis). The well-known epidemic of typhoid fever that occurred in Bournemouth in 1936 was eventually traced to infection of milk by churns which had been washed with sewage-polluted water. Fortunately, pathogenic bacteria have only a short life in water and are less resistant to adverse influences and more easily destroyed than either the normal intestinal bacteria or ordinary water bacteria. Hence it is inferred that if organisms of the *B. coli* group, which can easily be detected and counted, cannot be found, then the pathogens must also be absent. The predominant bacteria in sewage and river waters belong to the *coli*form group, and hence these organisms, though harmless in themselves, are used as test organisms in order to determine whether a water is safe bacteriologically (see Chapter 8).

It has recently been suggested by Allen that the use of *Streptococcus faecalis* as a second indicator organism may be advantageous in many cases, for instance in the examination of muds from sewage-polluted estuaries.

In tropical and semi-tropical countries, many dangerous diseases, such as amoebic dysentery (caused by the amoeba *Entamoeba histolytica*), leptospiral jaundice or Weil’s disease (caused by a spirochaete *Leptospira icterohaemorrhagiae*), can be caused by contaminated water. The ova and larvae of many worms are parasitic to man and may be passed out in the faeces and so contaminate water (see Chapter 8). This is not a serious problem in this country but is of great importance in most tropical countries. A list of the commoner pathogenic organisms found in sewage and polluted streams is given in Table 48 (Chapter 8).

The discharge of sewage and many organic trade wastes to a river often causes excessive growths of so-called ‘sewage fungus’ (see Chapter 8) which attaches itself as whitish or greyish tufts to stones on the river bed. The term really includes a number of organisms of which two common ones are the filamentous bacterium *Sphaerotilus natans* and the fungus *Leptomitus lacteus*. Conditions which favour the growth of sewage fungus are the presence of organic matter (nitrogenous organic matter, or carbohydrates in the presence of ammonium salts and nitrates), some dissolved oxygen (growth will not occur in the complete absence of dissolved oxygen), pH between about 7 and 8, and a fairly high temperature. Unfortunately, when sewage fungus dies, it undergoes decomposition usually with formation of hydrogen sulphide, and may thus become a real nuisance.

*Now usually called *Shigella dysenteriae*. There are several types of *Shigella* causing bacterial dysentery.*
INDUSTRIAL WASTES

In the highly industrialized areas of this country, such as Lancashire, the West Riding of Yorkshire, and the Midlands, many of the rivers and streams are polluted by a great variety of treated and untreated industrial waste waters. For example, the rivers within the area of the Mersey River Board (which covers the densely populated industrialized areas of Manchester and Liverpool) may contain waste waters from tanneries, fellmongers and leather dressers; food processing; rubber proofing; gas works; tar-distilling; electro-plating; iron pickling; coal-washing; sand-washing; quarrying; oil and grease processing and refining; the scouring of cotton and wool; the bleaching, finishing and mercerizing of cotton and rayon; the dyeing of cotton, wool, jute, and rayon; piggeries; slaughterhouses; calico-printing; and from the manufacture of batteries, paint, light alloys, rubber, plastics, rayon, dyes, chemicals, glue, gelatine, size, paper pulp and paper.

In the 9th Report of the Royal Commission on Sewage Disposal, trade waste waters are divided into the following three groups:

1. Wastes which are polluting mainly on account of the presence of suspended matter. Examples: waste waters from coal-washing, quarrying, and sand and gravel washing.

2. Wastes which are polluting partly because of the presence of suspended matter and partly on account of the presence of substances in solution. Examples: tannery, textile, dairy and beet-sugar wastes.

3. Wastes which are polluting mainly on account of the presence of substances in solution. Examples: gas liquor, electro-plating wastes, many chemical waste waters.

A more detailed classification of industrial waste waters has been given by Ettinger and this is shown, slightly modified, in Table 13. Each of these wastes can be further subdivided. For instance, cotton textile wastes may consist of cotton kiering, bleaching, mercerizing, dyeing, printing, and finishing wastes.

Table 13. Types of industrial waste waters

<table>
<thead>
<tr>
<th>Type of Waste Water</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Brine wastes</td>
<td>Water from saline deposits</td>
</tr>
<tr>
<td>2. Mineral washing slurries and suspensions (e.g. stone sawing, sand and china clay washing)</td>
<td>Water from mining activities</td>
</tr>
<tr>
<td>3. Mine drainage (pit water from coal mines)</td>
<td>Water from coal mining activities</td>
</tr>
<tr>
<td>4. Pickle liquor wastes (e.g. iron and copper pickling, galvanizing, etc.)</td>
<td>Water from metal processing activities</td>
</tr>
<tr>
<td>5. Electro-plating</td>
<td>Water from electro-plating activities</td>
</tr>
<tr>
<td>6. Water softening</td>
<td>Water from water treatment processes</td>
</tr>
<tr>
<td>7. Cooling water from condensers</td>
<td>Water from industrial exhaust systems</td>
</tr>
<tr>
<td>8. Boiler blow-off</td>
<td>Water from boiler systems</td>
</tr>
<tr>
<td>9. Inorganic chemical manufacturing wastes</td>
<td>Water from chemical manufacturing processes</td>
</tr>
<tr>
<td>10. Battery manufacture</td>
<td>Water from battery manufacturing</td>
</tr>
<tr>
<td>11. Coal-washing</td>
<td>Water from coal preparation processes</td>
</tr>
<tr>
<td>12. Inorganic pigments</td>
<td>Water from pigment production</td>
</tr>
</tbody>
</table>

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ASPECTS OF RIVER POLLUTION

Table 14—cont.

B. WASTES CONTAINING CHIEFLY ORGANIC MATERIALS

I. Hydrocarbon wastes

1. Oil wells
2. Petroleum refining
3. Styrene manufacture
4. Co-polymer rubber plants
5. Butadiene plants
6. Natural rubber processing or reclaiming
7. Petrol stations, garages, engineering works

II. Miscellaneous organic chemical wastes

8. Munition plants (e.g. TNT, Tetryl, ammonium picrate, etc.)
9. Synthetic pharmaceuticals
10. Synthetic or man-made textile fibers (e.g. rayon, nylon, etc.)
11. Organic chemical manufacture
12. Paints and varnishes
13. Oil and grease processing and refining

III. Phenolic wastes

14. Gas plants and by-product coke plants
15. Tar distillation, road oil, and creosoting plants
16. Chemical plants
17. Synthetic resin plants
18. Wood distillation
19. Dye manufacturing

IV. Biological wastes

(a) Wastes from processing of biological materials and/or from biological processes

20. Tanneries and leather trades
21. Pharmaceuticals (antibiotics, biologically; e.g. penicillin)
22. Alcohol industries (brewing and distilling)
23. Miscellaneous fermentation industries
24. Glue, size, and gelatine plants
25. Wool scouring
26. Textile manufacture (natural fibers; e.g. cotton, wool, silk, flax)
27. Fleece-cloth manufacture
28. Paper manufacture
29. Launderies

(b) Food processing wastes

30. Canneries
31. Meat packing, slaughterhouse, and related trades
32. Milk and dairy wastes
33. Corn products plants
34. Beet sugar factories
35. Cane sugar factories
36. Fish processing plants
37. Other food processing and dehydration plants

(c) Farm wastes (e.g. piggeries)

C. RADIOACTIVE WASTES

(e.g. atomic energy plants and experimental stations; hospitals using radioactive isotopes)

Some characteristic chemical substances present in trade wastes are shown in Table 14.
Table 14. Some chemical substances in industrial wastes

<table>
<thead>
<tr>
<th>Substances</th>
<th>Present in waste waters from</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free chlorine</td>
<td>Launderies, paper mills, textile bleaching</td>
</tr>
<tr>
<td>Ammonia</td>
<td>Gas and coke manufacture, chemical manufacture</td>
</tr>
<tr>
<td>Fluorides</td>
<td>Scrubbing of flue gases, glass etching, atomic energy plants</td>
</tr>
<tr>
<td>Cyanides</td>
<td>Gas manufacture, plating, case-hardening, metal cleaning</td>
</tr>
<tr>
<td>Sulphides</td>
<td>Sulphide dying of textiles, tanneries, gas manufacture, viscose rayon manufacture</td>
</tr>
<tr>
<td>Sulphites</td>
<td>Wood pulp processing, viscose film manufacture</td>
</tr>
<tr>
<td>Acids</td>
<td>Chemical manufacture, mines, iron and copper pickling, D.D.T. manufacture</td>
</tr>
<tr>
<td>Alkalis</td>
<td>Cotton and straw kiering, wool scouring, cotton mercerizing, laundries</td>
</tr>
<tr>
<td>Chromium</td>
<td>Plating, aluminium anodising, chrome-tanning</td>
</tr>
<tr>
<td>Lead</td>
<td>Battery manufacture, lead mines, paint manufacture</td>
</tr>
<tr>
<td>Nickel</td>
<td>Plating</td>
</tr>
<tr>
<td>Cadmium</td>
<td>Plating</td>
</tr>
<tr>
<td>Zinc</td>
<td>Galvanizing, zinc-plating, viscose-rayon manufacture, rubber processing</td>
</tr>
<tr>
<td>Copper</td>
<td>Copper-plating, copper pickling, cuprammonium rayon manufacture</td>
</tr>
<tr>
<td>Arsenic</td>
<td>Sheep-dipping</td>
</tr>
<tr>
<td>Sugars</td>
<td>Dairy, breweries, preserve manufacture, glucose and best sugar factories, chocolate and sweet industries</td>
</tr>
<tr>
<td>Starch</td>
<td>Food processing, textile industries, wall-paper manufacture</td>
</tr>
<tr>
<td>Fats, oils, and grease</td>
<td>Wood scouring, laundries, textile industries, petroleum refineries, engineering works</td>
</tr>
<tr>
<td>Phenols</td>
<td>Gas and coke manufacture, synthetic resin manufacture, textile industries, tanneries, tar distilleries, chemical plants, dye manufacture</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Synthetic resin manufacture, penicillin manufacture</td>
</tr>
</tbody>
</table>

HARMFUL EFFECTS OF SEWAGE AND TRADE WASTES

In this chapter, the effects of various kinds of pollution on streams have been discussed. By way of recapitulation, the more important harmful effects caused by the discharge of sewage and trade wastes to rivers can be briefly summarized as follows:

(i) Fermentable organic matter will decompose and cause de-oxygenation of the stream water. Fish may be asphyxiated and ultimately when all dissolved oxygen has disappeared there will be objectionable smells due to hydrogen sulphide, mercaptans, organic amines, etc. (page 21).

(ii) Suspended matter will deposit on the river bed, or behind weirs as sludge and cause silting up of the bed and possible flooding. If the suspended solids are largely organic in nature, putrefaction may occur, and solid matter buoyed up...
by gas may rise to the top, resulting in floating masses of evil-smelling and unsightly sludge. Suspended matter of any kind blankets the bottom of a stream, so interfering with the spawning of fish as well as reducing the number of animals which form the food of fish.

(iii) Corrosive substances (acids, alkalis) or toxic substances (e.g. cyanides, phenols, zinc, copper, etc.) may kill fish, bacteria, and other aquatic life, animal and vegetable. The resulting destruction of beneficial water bacteria may produce a sterile river which is unable to undergo natural self-purification. Such waters may prove dangerous to use for domestic purposes or for watering cattle.

(iv) Pathogenic micro-organisms may be discharged with sewage during epidemics (page 59). Trade wastes, as a rule, are free from pathogens, though anthrax bacilli may possibly occur in tannery wastes.

(v) Certain undesirable physical effects caused by the discharge of sewage and trade wastes are turbidity, discoloration, foam, and radioactivity. Heated effluents discharged to rivers (e.g. from power stations) may cause harmful rises in the temperature of the stream. This can lead to undesirable putrefaction in streams already polluted by organic matter, and may also cause destruction of fish in relatively unpolluted waters (pages 38-40).

(vi) Substances causing tastes and odours in water may be present in certain trade wastes (e.g. phenols, oil refinery wastes) and may make the water either unfit for drinking purposes or else difficult and costly to purify by conventional water purification processes (page 52).

(vii) Sewage and many organic trade wastes may cause excessive growths of sewage fungus (page 60) or other objectionable growths in a stream. These may choke the river bed or even the screens of river users, and may give rise to objectionable odours when they decompose.

(viii) Certain mineral constituents (e.g. calcium and magnesium) can cause excessive hardness in a river water, making it difficult to use for certain manufacturing processes. Excessive amounts of salt discharged to a stream may be objectionable if the chloride content of the stream rises to a value which is deleterious to freshwater fish and vegetation.

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CHAPTER 4

CAUSES OF RIVER POLLUTION

The cause taken away, the effect removeth.

GEORGE PETTIE.
Prote Palace, p. 193. 1576

Cause and effect, means and ends, seed and fruit,
cannot be severed; for the effect already blooms
in the cause, the end pre-exists in the means, the
fruit in the seed.

RALPH WALDO EMERSON.
Essay on Compensation. 1803-82

SEWAGE

The discharge of crude or partially treated sewage into a river constitutes by far the commonest form of pollution. The treatment and purification of sewage so as to render it fit for admission to a stream without causing pollution will be dealt with in a later chapter (see Chapter 12). It can, however, be stated here that in the absence of large proportions of inhibitory trade wastes the technical problems involved in the treatment of sewage have now been virtually overcome and by using one or more of the biological methods described in Chapter 12 it is possible to produce an effluent of a high degree of purity. Under certain circumstances where an even better effluent is required, this can be achieved by additional treatment of the normal final effluent, e.g. by the use of sand filters, micro-strainers, etc. (see Chapter 12). In normal cases where the dilution with good river water is at least eightfold, the Royal Commission on Sewage Disposal\(^1\) recommended that in order to avoid nuisance a sewage effluent should have a biochemical oxygen demand (B.O.D.) of not more than 20 p.p.m. and a suspended solids content not greater than 30 p.p.m. (cf. Chapter 14). Unfortunately, however, a large number of sewage disposal works which were formerly satisfactory cannot now conform to these standards of the Royal Commission. The works, perhaps, is very old and may have become seriously overloaded by additional sewage from new housing estates and possibly also by trade wastes, thus resulting in the production of effluents of a polluting character, i.e. effluents failing to pass the Royal Commission standards. Although the need for reconstructing or enlarging such works is obvious, yet the necessary extensions cannot always be carried out owing to the present Government restrictions on capital expenditure.
In cases where an entirely new works is needed to serve a new community, it is generally possible to get the necessary Ministry sanction for a loan.

A troublesome problem in many coal-mining areas (e.g. in parts of Lancashire) is mining subsidence which causes defects in the sewerage system (e.g. fractures of sewers, pipes, tanks, etc.). This results in crude sewage escaping to the river and causing pollution.

Sewage engineers do not consider it practicable to give complete treatment during wet weather to the whole of the sewage from combined or from partially separate sewerage systems. Since it is not practicable to construct sewers capable of carrying all storm water, it is necessary to have so-called 'storm overflows' on sewers to act as safety valves and take away at certain points on the sewerage system any excessive flows of sewage and storm water. These storm overflows are set in accordance with Ministry requirements to operate at six times the dry weather flow (D.W.F.). The usual practice, following the requirements of the Ministry of Housing and Local Government (formerly the Ministry of Health), is to give full treatment at the sewage works (i.e. settlement and biological purification) to $3 \times \text{D.W.F.}$, and partial treatment (i.e. settlement only) to flows between $3 \times \text{D.W.F.}$ and $6 \times \text{D.W.F.}$ (the settled liquor in the tanks being later passed through the works for full treatment). Flows in excess of $6 \times \text{D.W.F.}$, which occur after heavy storms, pass straight to the river without treatment. It is evident, therefore, that after every heavy rainstorm, untreated or partially treated sewage can pass from storm overflows and from sewage storm water tanks to the river, causing serious pollution particularly if the receiving stream is small.

These discharges to the river are liable to contain large amounts of suspended matter due to the flushing out of solid matter that has collected in sewers during relatively dry periods and to drainage from the scouring of roof and street surfaces. Evidence given before the Royal Commission on Sewage Disposal showed that storm water sewage after heavy rain had a very high content of suspended matter at the beginning of the storm and during the first few hours.

This is illustrated by Tables 15 and 16, taken from the Royal Commission Report.

* When the sewage contains a fair amount of infiltration water (i.e. ground water that has leaked into the sewers), the maximum amount to receive full treatment during a storm is $(3 \times \text{domestic sewage}) + (1 \times \text{infiltration water})$. When trade wastes are present in the sewage, full treatment is normally given to $(3 \times \text{domestic sewage}) + (1 \times \text{trade waste}) + (1 \times \text{infiltration water})$, but this is subject to modification according to local circumstances, since the allowance of 10 per cent made for the increase in flow of trade waste in wet weather has now been found to be quite inadequate.
CAUSES OF RIVER POLLUTION

Table 15. Suspended solids in Sheffield sewage during a storm (0.11 in. of rain)

<table>
<thead>
<tr>
<th>Time</th>
<th>Suspended solids p.p.m.</th>
<th>Time</th>
<th>Suspended solids p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before effects (of rainfall) were observed</td>
<td>592</td>
<td>4.50 p.m.</td>
<td>1,012</td>
</tr>
<tr>
<td>10.50 a.m.</td>
<td></td>
<td>5.50 p.m.</td>
<td>1,006</td>
</tr>
<tr>
<td></td>
<td></td>
<td>6.50 p.m.</td>
<td>979</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.50 p.m.</td>
<td>417</td>
</tr>
<tr>
<td>11.50 a.m.</td>
<td>602</td>
<td>8.50 p.m.</td>
<td>401</td>
</tr>
<tr>
<td>12.50 p.m.</td>
<td>671</td>
<td>Storm over-flow nearest</td>
<td></td>
</tr>
<tr>
<td>1.50 p.m.</td>
<td>1,761</td>
<td>9.50 p.m.</td>
<td>263</td>
</tr>
<tr>
<td>2.50 p.m.</td>
<td>1,259</td>
<td>the sewage works ceased</td>
<td></td>
</tr>
<tr>
<td>3.50 p.m.</td>
<td>1,335</td>
<td>operating</td>
<td></td>
</tr>
</tbody>
</table>

Comparison of the Heywood figures with the Royal Commission standard of 30 p.p.m. of suspended solids (page 71) shows that the first rushes contain nearly 80 times this quantity and that even after 7 hours the storm water contains 6 times this amount! Is it surprising, therefore, that much pollution of streams by sewage takes place after heavy rain?

Table 16. Suspended solids in Heywood storm water sewage (Heavy rain lasting 4 hours)

<table>
<thead>
<tr>
<th>Time sample was taken hours</th>
<th>Suspended solids p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>First rushes</td>
<td>2,380</td>
</tr>
<tr>
<td>After 1</td>
<td>1,100</td>
</tr>
<tr>
<td>After 2</td>
<td>690</td>
</tr>
<tr>
<td>After 3</td>
<td>500</td>
</tr>
<tr>
<td>After 4</td>
<td>380</td>
</tr>
<tr>
<td>After 5</td>
<td>330</td>
</tr>
<tr>
<td>After 6</td>
<td>280</td>
</tr>
<tr>
<td>After 7</td>
<td>180</td>
</tr>
</tbody>
</table>

The need for more thorough treatment of storm water before it is discharged to a river has been stressed by Garnier. He reports that at eleven sewage disposal works where storm water was treated in tanks constructed to meet the requirements of the Ministry, the average suspended solids figure for 23 samples was 300 p.p.m. (or 10 times the Royal Commission standard!) whilst the maximum figure was 950 p.p.m. and the minimum 60 p.p.m. He adds: 'I think that no one will dispute that storm water is receiving insufficient treatment. I would advise all local authorities when constructing new works to make ample provision for storm water and not to be content with the minimum required by the Ministry...'
It does on the face of it seem illogical to require a fairly strict standard of purity for a sewage effluent during dry weather and to have no standard at all for part of the flow during a storm. It could be argued that dilution of a stream during heavy rain might offset any pollution caused by storm water sewage or storm overflows but in practice it is found that the river during flood conditions is often in a worse state than during dry weather. In this connection, Clay, a rivers inspector of long experience, writes: 'A somewhat disquieting feature in this country is the fish mortality which occurs as a result of storms, particularly those following long periods of dry weather; creating intense waves of pollution during which the water might be almost totally devoid of dissolved oxygen and contain an abnormally high amount of suspended solids.'

There is no doubt that many storm overflows are set far too low. Indeed, there are some that operate for most of the year even in dry weather! Many were set and designed for flows that have subsequently increased enormously and any raising of the setting might lead to surcharge of the sewers and flooding. In such cases, there is little one can do short of providing a completely new sewerage system, which, in most cases, is ruled out by the high cost.

The recommendations of the Royal Commission on Sewage Disposal with regard to the height at which storm water overflows on sewers should be set are as follows:

'Storm overflows on branch sewers should be used sparingly and should usually be set so as not to come into operation until the flow in the branch sewer is several times the maximum normal dry weather flow in the sewer. No general rule can be laid down as to the increase in flow which should occur in the branch sewers before sewage is allowed to pass away by the overflow untreated. The Rivers Board... should have power to require the Local Authority to alter any storm overflow which, in their opinion, permit of an excessive amount of unpurified sewage to flow over them... The general principle should be to prevent such an amount of unpurified sewage from passing over the overflow as would cause nuisance.'

A feature of these recommendations is their flexibility and there is little doubt that the commission intended that local circumstances should be taken into account when fixing the height at which storm overflows should be set. It must be remembered, too, that conditions have undergone some change since the Royal Commission made its report. For instance, Stanbridge has pointed out that the run-off of rain from present-day impervious road surfaces is much faster than it used to be and consequently it may happen that a river is called upon to receive storm water from the sewers and
sewage works before its own volume has increased due to natural drainage from its catchment basin. 1

The present view of the Ministry is that overflows on sewers should be fixed so as to operate when 6 times the average D.W.F. of sewage (neither more nor less!) is passing down the sewer. This figure of $6 \times D.W.F.$ seems to be regarded by the Ministry as a kind of inviolable entity apparently intended to be applied without due regard to the dilution afforded by the receiving stream, to the strength of the sewage, or to other local circumstances. Nevertheless, there have been cases in the past where the Ministry has given way after pressure from a river board or local authority and agreed, in order to avoid pollution, to a higher setting of storm overflows than $6 \times D.W.F.$ or even that they shall operate only infrequently, and to partial treatment at the sewage works of storm water sewage in excess of $6 \times D.W.F.$ At the West Middlesex (Mogden) sewage works, a works with a large drainage area, the sewerage system is so extensive that a balancing effect is produced in consequence of which the storm overflows on sewers rarely come into operation and very little use is made of the storm water tanks. At Knutsford, Cheshire, where the sewage effluent discharges to a small trout fishing stream (the Birkin brook), it was considered necessary in order to avoid damage to the fishery to set the storm overflows at no less than $14 \times D.W.F.$, and to give full treatment to $6 \times D.W.F.$ and partial treatment to flows between $6 \times D.W.F.$ and $14 \times D.W.F.$ At the new Swinton and Pendlebury (Clifton) sewage works, partial treatment in storm water tanks is given to flows between $3 \times D.W.F.$ and $8 \times D.W.F.$, whilst at the new Whiston R.D.C. (Rainhill) sewage works, the effluents from which discharge to a small stream, storm tank treatment will be given to flows between $3 \times D.W.F.$ and $12 \times D.W.F.$

It is now becoming increasingly difficult, no doubt for financial reasons, to get Ministry sanction for storm overflow settings greater than $6 \times D.W.F.$ or for the partial treatment in storm tanks of more than $6 \times D.W.F.$ There is, nevertheless, little doubt that the provision of more generous settings for storm overflows and of sufficient storm tank capacity to permit partial treatment of flows in excess of $6 \times D.W.F.$ (the exact amount being decided by local circumstances) would do much towards the abatement of stream pollution. The extra cost of doing this would in most cases be small in comparison with the benefits obtained. For a further discussion of the problem of storm overflows, the reader is referred to Lover's recent paper.

A technical committee set up by the Ministry of Housing and Local Government is at present engaged upon a study of the problems and practice relating to storm overflows on sewers and to the
disposal of storm water. An up-to-date report on this subject is awaited with great interest.

Most of the sewage disposal works in this country are constructed on the combined system. There is a tendency, nowadays, to use the separate system for some of the newer works in an attempt to avoid pollution caused by storm overflows and by storm water sewage. In this way, cleaner water finds its way to the stream during a storm. Unfortunately, the separate system of sewage is more costly to construct since separate sewers are required for sewage and surface water. In South Africa, the prevalence of sudden and intense rainstorms makes the use of the separate system necessary.

Much pollution is sometimes caused in built-up areas by repairs to sewers, thus necessitating temporary diversion of crude sewage (often containing trade wastes) to the nearest watercourse. This is particularly liable to happen when the sewers are very old or when they are receiving corrosive trade wastes and it is difficult to suggest a remedy for this state of affairs.

In many unsewered rural areas and even in some unsewered urban areas, there may be a large number of isolated houses provided with septic tanks (see Chapter 12) as the sole means of sewage treatment. Since septic tanks produce unsatisfactory effluents which do not comply with the standards for sewage effluents proposed by the Royal Commission on Sewage Disposal (see this chapter, page 71), much pollution of the smaller watercourses is caused in many of these areas, resulting in smells and constituting in some instances a potential danger to public health. It would, therefore, seem highly desirable that the planning authority should take appropriate action to prevent the building of such isolated properties unless proper sewage disposal facilities are provided, and that the construction of groups of houses should be accompanied by the provision of proper sewerage and sewage disposal works under the supervision of the local authority.

TRADE WASTES

Next in importance to sewage as a cause of stream pollution, and, indeed, rivalling sewage in certain districts, is the discharge of waste waters from trade premises. In such densely populated and highly industrialized areas of England as south Lancashire, the West Riding of Yorkshire, and the Midlands, many watercourses once famous for their fishing have become so polluted by trade discharges that they have become virtually dead rivers incapable of supporting animal or vegetable life. An outstanding example of such a stream is the notorious River Irwell, draining a densely populated area which
includes the twin cities of Manchester and Salford. In this connection, I cannot do better than quote the picturesque description of this river given by Hazeldine. 10.

'... even the Irwell which drains one of the most industrialized areas in the world begins its meanderings as a pure pellucid babbling brook and can be likened to a beautiful virgin maid. But what has happened to our fair maid, who at Irwell Springs was as God made her, but by the time she forms the Manchester Ship Canal above Trafford Bridge is a weary, forlorn and morally bedraggled hussy as man left her. To begin with, on the up-reaches of the river and its tributaries many years ago, the ancient bleachers, dyers, calico printers and finishers of textile goods staked their works and established their right to impound the necessary clean water required for their trade processes. Thus the fair maiden does not travel very far before her hair is dyed blue, green, or some other unnatural colour; her eyes are burned by acids or caustic soda and her skin befouled by starch and china clay. Fellmongers, tanners; tar distillers, paper makers, bone boilers, chemical manufacturers, gas works, sewage works and many others gleefully add to her discomfiture.'

It is possible to treat many trade wastes by methods which will be discussed later (see Chapter 13), so as to produce a reasonably satisfactory effluent, which, given sufficient dilution in the river, will not cause pollution. There are, however, many trade wastes for which no large-scale methods of treatment of proved reliability has been developed (e.g. gas liquor, and kier liquors) or for which only methods of partial purification are available. In such cases, advantage can sometimes be taken of the Public Health (Drainage of Trade Premises) Act, 1937 (see Chapter 2, page 14, also Chapter 13, page 488) and, with the consent of the local authority, the waste waters can be discharged to the public sewers, subject to certain conditions and safeguards, for biological treatment in admixture with sewage at the sewage disposal works. Amongst the many benefits of this method of disposal are the following:

(i) It is easier and less costly, as a rule, to purify a mixture of sewage and trade wastes than to deal with the trade wastes separately.

(ii) At a sewage works of sufficient capacity, it is usually possible to obtain from the mixed sewage and trade wastes a final effluent conforming to Royal Commission standards (page 71) whereas this is rarely possible by the separate treatment of industrial wastes.
(iii) There is a reduction in the number of points of pollution on the river.

(iv) There is skilled technical supervision at a sewage works of any size by staff specially trained for the job. Such expert supervision is unlikely to be obtained at any but the largest industrial plants.

(v) It eliminates the accidents that sometimes occur at trade waste purification plants through carelessness, leakages, lack of adequate technical control of the processes, and breakdown of pumps and other vital parts of the plant.

The question of the treatment of trade wastes in admixture with sewage is of such importance that it will receive further discussion later (see Chapter 13). Unfortunately, this convenient and generally satisfactory method of dealing with a trade effluent problem is not always practicable for many reasons. It may happen that no sewers are available within a reasonable distance of the trade premises, or that the nearest sewers are not large enough. In either case, the cost of laying a new sewer might prove prohibitive. Also, if the local sewage works is of insufficient capacity, it may be unable to accept any additional load either of a strong waste or of a large volume of more dilute wastes. Even if such difficulties could be surmounted by extensions to the sewage disposal works, it is not always easy in these times of financial stringency to obtain the necessary Ministry sanction for a loan. In some instances, especially where the stream consists mainly of trade effluents in dry weather, disposal of wastes to the sewers might cause trouble with riparian owners* downstream who could reasonably object to being deprived of the water (even if it is dirty water!) to which they have a legal right.

Pollution is sometimes caused by trade wastes for which no reasonably practicable method of producing a satisfactory effluent is known, and which cannot be disposed of to the local sewers for one of the reasons already advanced. The problem is accentuated if the stream into which the effluent discharges is a small one affording little dilution in dry weather. In certain heavily industrialized and densely populated areas (e.g. South Lancashire) where there are a great variety of industrial wastes many of which are difficult to treat, stream pollution is particularly hard to control on account of the large number of closely separated points of pollution, the smallness of the rivers, and the lack of sufficient clean dilution water. A fuller discussion of the many problems arising in such areas is given in a paper by the author**. A peculiarly difficult

* A riparian owner (from Latin riparius — belonging to a bank or shore) possessing land bordering on a stream has certain legal rights regarding the banks, stream bed, and waters (e.g. reasonable use of the water). Cf. Chapter 2, page 15.

** A paper by the author.
problem exists when a firm situated on the head waters of a stream
impounds all or most of the water which is subsequently used for
process work and is finally discharged as a trade effluent. Even if
the effluent is treated by the best practicable means and is "satis-
factory" on the basis of certain arbitrary standards, it cannot be
satisfactory considered as a river water. It is possible that some
form of treatment of the river itself (e.g. by aeration) may offer a
solution of this difficulty (cf. Chapter 15, pages 572-3).

MINE WATER
A peculiar form of river pollution arises from water associated with
coal-mining, including water pumped from abandoned mines.
This 'mine drainage' or 'pit water' is usually low in organic matter
but contains considerable amounts of ferrous and ferric salts
(mainly as sulphates), sulphates of aluminium, calcium and mag-
nesium and often free sulphuric acid. The iron compounds and
the acid are usually assumed to originate from the atmospheric
oxidation of iron pyrites (FeS₂) which is generally associated
with coal. It is also possible that the high acidity of some mine
waters may be due to bacterial action by sulphur-producing organ-
isms. This is supported by recent American work 11,12 which
appears to show that not only the formation of sulphuric acid but
also the oxidation of ferrous sulphate to ferric sulphate may be
bacteriological processes involving the participation of sulphur-
bacteria and iron-bacteria. The presence of sulphur-oxidizing
bacteria and iron-oxidizing bacteria in acid mine waters lends
additional support to these views. Moreover, the addition of disinfec-

tants prevents the development of the characteristic ochre
colour even when air is present. Other bacteria have been found
to withstand the very acid conditions associated with mine waters.
Thus, the work of Joseph and Shav13 on the viability of Esch. coli* in
such waters has shown that although most of the bacteria were
killed, nevertheless the acid conditions were not sufficient to ensure
complete destruction of the bacteria.

A few analyses of mine waters from Lancashire mines are shown
in Table 17.

Mine waters containing ferrous iron are particularly objectionable
in a river since ferrous compounds are strong reducing agents and
so tend to denude the stream of its dissolved oxygen. Moreover,
such waters tend to encourage the growth of filamentous iron
bacteria 14,15 which flourish in acid waters containing iron and
some organic matter. These bacteria possess the faculty of

* i.e. Bact. coli 1, a normal inhabitant of the human intestine and present in large
numbers in sewage.
oxidizing soluble ferrous salts to ferric compounds, resulting in the accumulation of slimy reddish-brown deposits containing the bacteria and ferric hydroxide. Water undertakings sometimes suffer considerably in this way for these deposits can cause blocking up of pipes and the unsightly rusty-coloured water stains wash-basins, baths, etc. In addition, death of the bacteria leads to the production of offensive odours. SCRIBER believes that the turbidity caused by the oxidation of ferrous iron can, by cutting off light, prevent animal life from establishing itself at the bottom of the stream. Other objectionable effects of mine waters on a stream are reduction in pH value (which may cause fish mortality), precipitation of iron compounds, and increases in total hardness, iron, and sulphate. The acid in mine water also tends to reduce markedly the normal bacterial flora of a stream and so may cause a fall in the rate at which self-purification takes place.

Analytical data showing the effect of pollution by mine water on a Lancashire stream are given in Table 18.

A particularly objectionable feature of mine water pollution is the precipitation of ferric hydroxide, which can vary in colour from yellow to reddish-brown, when the acidity of the mine water is neutralized by the natural bicarbonate alkalinity of the stream, thus giving the stream water as well as the bed and banks an ‘ochre’ colour. Hence the name ‘ochre water’ generally given to such mine waters. These conditions occur in the River Don for some distance below Sheffield and in many streams in Yorkshire.

<table>
<thead>
<tr>
<th></th>
<th>No. 1</th>
<th>No. 2</th>
<th>No. 3</th>
<th>No. 4</th>
<th>No. 5</th>
<th>No. 6</th>
</tr>
</thead>
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<td>pH value</td>
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<td>3-8</td>
<td>6-3</td>
<td>6-7</td>
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<td></td>
<td></td>
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<tr>
<td>$\text{K}_2\text{MnO}_4$</td>
<td>37-2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>326</td>
</tr>
<tr>
<td>in 3 min p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxygen absorbed from</td>
<td>37-4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>338</td>
</tr>
<tr>
<td>$\text{K}_2\text{MnO}_4$ in 4 h p.p.m.</td>
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<td></td>
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</tr>
<tr>
<td>Total solids</td>
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<td>4,240</td>
<td>5,640</td>
<td>4,910</td>
<td>1,727</td>
<td>20,220</td>
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<td>p.p.m.</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Suspended solids</td>
<td>185</td>
<td></td>
<td></td>
<td>44</td>
<td>44</td>
<td>44</td>
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<tr>
<td>Alkalinity to methyl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>orange p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>of $\text{CaCO}_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acidity to methyl</td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>orange p.p.m. of</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{CaCO}_3$</td>
<td>nil</td>
<td>nil</td>
<td>15</td>
<td>nil</td>
<td>nil</td>
<td>647</td>
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<td>$\text{Volatilized Na}_2\text{SO}_4$</td>
<td></td>
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<tr>
<td>Ferrous iron</td>
<td>290</td>
<td>145</td>
<td>11</td>
<td>67</td>
<td>67</td>
<td>2305</td>
</tr>
<tr>
<td>p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ferric iron</td>
<td>10</td>
<td>230</td>
<td>nil</td>
<td>64</td>
<td>16</td>
<td>238</td>
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<td>p.p.m.</td>
<td></td>
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<tr>
<td>Total hardness</td>
<td>1,840</td>
<td>3,390</td>
<td>870</td>
<td>605</td>
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<td>p.p.m. of $\text{CaCO}_3$</td>
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</tr>
<tr>
<td>Sulphate</td>
<td>1,560</td>
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<td>p.p.m. of $\text{SO}_4$</td>
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<tr>
<td>Chloride</td>
<td>72</td>
<td>32</td>
<td>67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p.p.m. of Cl</td>
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<td></td>
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</tr>
<tr>
<td>Ammonia nitrogen</td>
<td>0-06</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Albuminoid nitrogen</td>
<td>4-7</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p.p.m.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total hardness</td>
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<td>2-36</td>
<td>2-36</td>
<td>2-36</td>
<td>2-36</td>
</tr>
<tr>
<td>p.p.m. of $\text{CaCO}_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphate</td>
<td>6-4</td>
<td>6-4</td>
<td>6-4</td>
<td>6-4</td>
<td>6-4</td>
<td>6-4</td>
</tr>
<tr>
<td>p.p.m. of $\text{SO}_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
CAUSES OF RIVER POLLUTION

Lancashire and other coal-mining districts. These ochre deposits can thus originate in three different ways:

(i) chemical oxidation by dissolved oxygen of ferrous compounds to insoluble ferric hydroxide;
(ii) by ingress of alkaline surface waters;
(iii) biochemical oxidation of ferrous compounds to ferric hydroxide by the action of iron bacteria.

Unfortunately, it is by no means easy to control pollution of rivers by mine water since in this country the National Coal Board is protected against any action by river boards under Section 2 of the Rivers (Prevention of Pollution) Act, 1951, which exempts water raised or drained from any underground part of a mine so long as it is in the same condition as when it was so raised or drained. It is possible, however, to take proceedings against the National Coal Board under the Alien and Freshwater Fisheries Act, 1923, in cases of pollution of a fishing stream by mine water if the discharge can be proved to be injurious to fish or to fish food.

In County Durham, there is an interesting example of the use of mine water for domestic supplies18, 19. At the New Brancepeth Colliery, the Sunderland and South Shields Water Co. treat 1,000,000 gal. per day of mine water containing 0·3 p.p.m. of iron and 0·7 p.p.m. of manganese by aeration, superchlorination and filtration, to remove iron and manganese.

### Table 18. Effect of mine water pollution on a Lancashire stream

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Stream before receiving mine water</th>
<th>Stream after receiving mine water</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH value</td>
<td>7-4</td>
<td>3-8</td>
</tr>
<tr>
<td>Chloride, as Cl</td>
<td>59 p.p.m.</td>
<td>36 p.p.m.</td>
</tr>
<tr>
<td>Oxygen absorbed from 80% KMnO₄ in 3 min</td>
<td>0·7 p.p.m.</td>
<td>1·4 p.p.m.</td>
</tr>
<tr>
<td>Oxygen absorbed from 80% KMnO₄ in 12 h</td>
<td>4·4 p.p.m.</td>
<td>4·6 p.p.m.</td>
</tr>
<tr>
<td>Alkalinity to methyl orange p.p.m. of CaCO₃</td>
<td>110 p.p.m.</td>
<td>nil</td>
</tr>
<tr>
<td>Acidity to methyl orange p.p.m. of CaCO₃</td>
<td>nil</td>
<td>30 p.p.m.</td>
</tr>
<tr>
<td>Ammoniacal nitrogen</td>
<td>0·44 p.p.m.</td>
<td>nil</td>
</tr>
<tr>
<td>Albuminoid nitrogen</td>
<td>3·4 p.p.m.</td>
<td>0·5 p.p.m.</td>
</tr>
<tr>
<td>B.O.D. (3 days, 20°C)</td>
<td>88 p.p.m.</td>
<td>86 p.p.m.</td>
</tr>
<tr>
<td>Dissolved oxygen per cent of saturation</td>
<td>651 p.p.m.</td>
<td>1,012 p.p.m.</td>
</tr>
<tr>
<td>Total solids</td>
<td>24 p.p.m.</td>
<td>171 p.p.m.</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>21 p.p.m.</td>
<td>81 p.p.m.</td>
</tr>
<tr>
<td>Nitrate nitrogen</td>
<td>4·5 p.p.m.</td>
<td>252 p.p.m.</td>
</tr>
<tr>
<td>Ferrous iron</td>
<td>6·4 p.p.m.</td>
<td>4·4 p.p.m.</td>
</tr>
<tr>
<td>Ferric iron</td>
<td>8 p.p.m.</td>
<td>100 p.p.m.</td>
</tr>
</tbody>
</table>

Unfortu
ASPECTS OF RIVER POLLUTION

In the U.S.A., much damage has been done by mine drainage in streams covered by the Ohio River Basin coalfields, especially in Pennsylvania and West Virginia. Neutralization of the acidity of the mine water is not considered practicable for financial reasons but something has been done to alleviate the pollution by sealing the openings of abandoned and active mines, and by controlling the flow of river water (e.g. by impounding relatively alkaline stream water above the mines and releasing it during periods of low stream flow to avoid too high an acidity in the mixture of river and mine drainage).

NATURAL POLLUTION

Pollution of rivers may take place as a result of natural causes not necessarily associated with the activities of man. Pollution of this kind is generally small and intermittent, being often connected with adverse weather conditions (e.g. heavy rain, a sudden thaw, etc.). Hence, it may consist of run-off from land carrying silt, vegetable matter, manure, etc., washed into the river during a storm. The extent and character of such pollution depend on the chemical and physical characteristics of the river bed and catchment area and on the type of vegetation present. Erosion of river banks and of valley slopes can lead to considerable natural pollution. The kinds of pollution commonly found in streams as a result of natural causes include organic matter, mineral matter, suspended matter, turbidity, colour, odour, acidity and alkalinity. For instance, in limestone areas, the pollution may consist of hardness and the water may be somewhat alkaline. Drainage from peaty areas is liable to contain much vegetable matter, colour, and organic acids. Jee has recorded that a cloudburst in the Upper Eden valley in 1930 caused pollution by peaty matter downstream to such an extent that large numbers of trout were killed.

In many rivers, especially sluggish industrial rivers, heavy rain with consequent high river flows, produces a scouring effect, causing sludge on the river bed and behind weirs, dams, etc. (which is often in a septic condition) to be stirred up. Samples of river water taken under these conditions have an abnormally high content of suspended solids.

A peculiar kind of natural pollution which has been known for a long time is the sudden appearance in lakes, ponds, reservoirs, streams, and even the sea, of excessive growths (so-called 'blooms') of algae. Certain blue-green algae are particularly liable to cause trouble in this way but it can also occur with some of the red and brown algae. This phenomenon has caused much trouble in the U.S.A., where lakes are often used for the disposal of sewage.
The various factors influencing the formation of algal blooms have been very thoroughly discussed by Sawyer and include climate, such physical factors as lake area, shape and depth, prevailing winds and their intensity, and chemical factors such as pH, presence of carbon dioxide, and of inorganic nutrients (especially nitrogen and phosphorus). Algal blooms can also occur in this country, more particularly in reservoirs in which slightly alkaline waters containing bicarbonates as well as organic impurities are stored (e.g. the waters of the Rivers Thames and Lee). Algal blooms are associated with the presence of fairly high concentrations of certain nutrient materials (especially nitrates and phosphates) found in sewage effluents which stimulate the growth of algae particularly under conditions of excessive sunshine and warmth. Eventually, the algae undergo decomposition and so can cause damage to fisheries, presumably by depleting the water of its dissolved oxygen and possibly also by the formation of substances toxic to fish. Tastes and odours may also be imparted to the waters and this is particularly undesirable if the water is to be used for drinking purposes. Chemicals can be used to destroy such algal growths and copper sulphate and chlorine, separately or in combination, are commonly employed for this purpose. According to Fair and Whipple, most algae are killed by as little as 0.05-0.5 p.p.m. of copper sulphate but a few may require as much as 10 p.p.m. When fish are present, care must be taken to use as small a quantity of copper sulphate as possible since fish are easily killed by traces of copper compounds. A laboratory test to determine the most effective dose of copper sulphate in the control of algae has been described by Montg. FitzGerald and his co-workers have discovered that 2,3-dichloronaphthoquinone is lethal to blue-green algae in a concentration as low as 0.002 p.p.m. when the algae are exposed to the action of this chemical for 10 minutes in light. Preliminary experiments have shown that this compound is not toxic either to fish, to most green algae, or to other aquatic organisms at this concentration or even at a concentration of 0.1 p.p.m. Large scale field tests in a lake containing fish have confirmed the results of the laboratory experiments.

Excessive growths of weeds and other vegetable life sometimes take place in rivers and they not only cause an obstruction of the free flow of the river but when they die and decay can seriously deplete the river of its dissolved oxygen. Whilst in this country mechanical removal of weeds is generally favoured, in the U.S.A. chemical control of aquatic growths has sometimes been practised using such substances as sodium chlorate, salts of 2,4-dichlorophenoxyacetic acid, and sodium arsenite. Care is needed...
in the application of these toxic chemicals since they may cause mortality amongst fish, and, of course, they are inapplicable if the water is to serve for drinking purposes.

USE OF TOXIC CHEMICALS FOR AGRICULTURAL AND OTHER PURPOSES

During the past few years, many new synthetic organic insecticides and herbicides have found increasing and extensive application for agricultural and other purposes. Unfortunately, some of these compounds are extremely toxic to fish and the possibility cannot be overlooked that the widespread use of these substances as pesticides and weed-killers might cause pollution of streams especially after rain. Indeed, Ward has reported that in surface waters of South-west Oklahoma heavy losses of fish occurred after cotton fields had been sprayed with insecticides containing aldrin and toxaphene; apparently toxic concentrations of aldrin can persist in streams for many days. Reference to the risks attached to the agricultural use of weed-killers is made in an annual report of the Nene River Board and two examples of fish mortality caused in this way are mentioned. The Board adds: 'The answer to this particular danger seems to be greater care in preparation and handling of these substances, clearing of all residues and containers after use and better education of farmers in the risks involved.'

Some idea of the extreme toxicity of many of these compounds can be obtained from Table 19 which lists some of the more important of these newer organic chemicals used as herbicides and insecticides. The lethal concentrations to fish given in the table are only very approximate but do serve as a rough guide to the order of magnitude of the figure (page 29).

Some of these insecticides (especially DDT and BHC) are occasionally used at a sewage disposal works to control flies associated with biological filters. The amounts used are probably too small to affect fish in the stream receiving the sewage effluent but the position needs careful watching.

MISCELLANEOUS CAUSES OF RIVER POLLUTION

The damaging effects on rivers of intermittent pollution by sewage from storm overflows, and by storm tank sewage, have already been discussed earlier in this chapter (page 72). There are, in addition, a variety of potentially polluting liquors, drainings, and sludges produced at a sewage disposal works. Hurley has humorously pointed out that, in the old days, 'many such unwanted trifles were
### Table 19. Some synthetic toxic organic chemicals used as herbicides and insecticides

<table>
<thead>
<tr>
<th>Commercial or common name</th>
<th>Chemical name</th>
<th>Use</th>
<th>Remarks</th>
<th>Approximate harmful concentration to fish, p.p.m.</th>
<th>Reference (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-D</td>
<td>2,4-dichlorophenoxyacetic acid</td>
<td>Herbicide</td>
<td>Used for weed control. Toxic to non-grassy plants</td>
<td>500* (sardine and cat-fish) 1,500* (minnows)</td>
<td>36</td>
</tr>
<tr>
<td>Santobrite</td>
<td>Sodium pentachlorophenate</td>
<td>Herbicide</td>
<td>Controls broad-leaved weeds</td>
<td>0-2</td>
<td>37</td>
</tr>
<tr>
<td>DDT</td>
<td>2,2-bis-(p-chlorophenyl)-1,1,1-trichloroethane</td>
<td>Insecticide</td>
<td>Kills flies and mosquitoes. Controls flies at sewage works filters</td>
<td>&gt;0-1 (goldfish)</td>
<td>38, 39</td>
</tr>
<tr>
<td>BHC (gamma-Hexachlorocyclohexane)</td>
<td>y-hexachlorocyclohexane (y-isomer of benzene hexachloride)</td>
<td>Insecticide</td>
<td>Kills flies and mosquitoes. Controls flies at sewage works filters</td>
<td>0-035</td>
<td>40</td>
</tr>
<tr>
<td>TEPP</td>
<td>Tetrachlor Pyrophosphate</td>
<td>Insecticide</td>
<td>One of the most toxic insecticides</td>
<td>About 0-005 (trout)</td>
<td>41, 42</td>
</tr>
<tr>
<td>Aldrin</td>
<td>Hexachloro-hexahydrodimethano-saphthalene</td>
<td>Insecticide</td>
<td>A highly toxic compound</td>
<td>About 0-02</td>
<td>42</td>
</tr>
<tr>
<td>Parathion</td>
<td>O,O-dimethyl O-p-nitrophenyl phosphorothionate</td>
<td>Insecticide</td>
<td>Effective against a wide range of insects and mites</td>
<td>About 0-2 (bluegills)</td>
<td>41</td>
</tr>
</tbody>
</table>

* Maximum safe concentration.
on some of the normal sewage purification processes. For instance, supernatant liquor can upset the sedimentation of sewage, and humus sludge sometimes causes trouble with 'rising sludge' in primary sedimentation tanks.

There are many other miscellaneous discharges, occasional or continuous, which may have a bad effect on the quality of river water or may make it difficult or even impossible for fish and other river life to establish themselves or even to exist at all. Examples of such pollutions are solid pollution, oil pollution, drainage from various tips, pea vine drainage, seepage from silos, drainage from farms and manured land, surface and road drainage, sludge from mill dams, boiler blow-off water, pollution resulting from sheep dipping and watering cattle in streams, accidental pollution, and unknown discharges. These merit further consideration.

SOLID POLLUTION

Pollution discussed under various headings in the previous chapter has been liquid, with or without solid material in suspension. Pollution can also be caused by the dumping of solid refuse, rubbish, or litter into a river, or by the placing of such solid matter so that it drains or passes into the river. The aesthetic value of a stream, especially in built-up and industrialized areas, is often much spoilt (1) by the thoughtless actions of persons, including children, who throw rubbish of all kinds into the water, and (2) by manufacturers who tip their sludge and other solid wastes on or near the river bank so that there is serious encroachment on to the river by the tip with the probable result that part of the tip may be carried into the water during wet weather. These practices, besides causing pollution, may well lead to considerable erosion of the opposite bank as well as to shoal formation farther downstream.

In the various general and local anti-pollution Acts passed prior to 1951, pollution by solid matter was regarded as being in a different category from pollution by liquid matters (which include solids in suspension). There was, for example, a definite prohibition of the putting of any kind of solid matter into a stream in Section 43 of the Lancashire County Council (Rivers Board and General Powers) Act, 1938, part of which reads as follows:

'Every person who:
(a) puts or throws or causes to be put or thrown or to fall; or
(b) knowingly permits to be put or to fall or to be carried; or
(c) causes or knowingly permits to be put in such a position as to be liable to fall or to be carried by floods; into any stream within the district of the Board the solid refuse of, or the sweepings from any factory manufacturing process.
brickyards, mine pits, shafts, quarries, shops, houses, farms, or roads or any bricks, gravel, sand, soil, ashes, cinders or clinkers, or any building or other rubbish or any sludge or any solid sewage matter or any vegetable or other garbage or offal or the carcass or a portion of the carcass of any animal or any other solid matter whatsoever whether in a dry or wet state shall be guilty of an offence against this Act. . . .

The Rivers Pollution Prevention Sub-Committee of the Central Advisory Water Committee recommended that the Lancashire section should be adopted in new legislation—a recommendation which evidently did not commend itself to the Minister of Housing and Local Government. In the Rivers (Prevention of Pollution) Act, 1951, which superseded the earlier Acts, no definite distinction is made between solid matters and liquid matters, and a person commits an offence under this Act if he 'causes, or knowingly permits to enter a stream any poisonous, noxious or polluting matter'—whether this be liquid or solid. If, however, the matter is of a solid nature, then it is necessary, in order to obtain a conviction under the Act, to show that pollution is being caused, unless by-laws are made (under Section 5 of the 1951 Act) making the putting of litter into streams an offence.

**OIL POLLUTION**

Oil pollution is usually occasional or intermittent and the result of accidental discharges from garages, engineering works, etc. It can, however, occur as a consequence of the use of rivers and canals by ships and barges for navigation.

**TIP DRAINAGE**

Tips can consist of municipal refuse as well as miscellaneous solid waste products of little or no commercial value from coal mines, manufacturing processes, and trade effluent treatment plants. Although the dumping of solid wastes and sludges on land is unavoidable in many cases, care must be taken that the tips are not sited too near a stream since during wet weather the drainage may cause serious pollution. Sometimes the drainage from municipal refuse tips contains organic matter having a high B.O.D. and by denuding a stream or other body of water of dissolved oxygen has been the cause of mortality amongst fish.

Many chemical tips have existed for a very long time and their removal might prove difficult and costly. Drainage from these old waste heaps is frequently of a polluting character and may contain such substances as acids, alkalis, chromates and sulphides.
ASPECTS OF RIVER POLLUTION

Colliery tips are liable to contain iron pyrites (FeS₂). The weathering of this mineral, according to Mapstone, give rise to ferrous sulphide, sulphur dioxide, ferrous sulphate, sulphuric acid, hydrogen sulphide, and free sulphur in accordance with the following equations:

\[
\begin{align*}
\text{FeS}_2 + O_2 & = \text{FeS} + \text{SO}_2 \\
\text{FeS} + 2\text{O}_2 & = \text{FeSO}_4 \\
2\text{SO}_2 + \text{O}_3 + 2\text{H}_2\text{O} & = 2\text{H}_2\text{SO}_4 \\
\text{FeS} + \text{H}_2\text{SO}_4 & = \text{FeSO}_4 + \text{H}_2\text{S} \\
2\text{H}_2\text{S} + \text{SO}_2 & = 3\text{S} + 2\text{H}_2\text{O}
\end{align*}
\]

It is obvious that drainage from colliery tips, which bears some resemblance to mine water in composition, can be of a very polluting character. Many of these colliery tips are liable to fire spontaneously but attempts to extinguish the fire by spraying with water can increase the pollution from the highly acid drainage. Every care should, therefore, be taken to avoid as far as possible the inclusion of coal in these tips.

A river board has the power under Section 3 of the Rivers (Prevention of Pollution) Act, 1951, to apply to the County court for an order prohibiting the use of land for any kind of tipping which causes or is likely to cause pollution of a stream.

PEA VINING DRAINAGE

In many agricultural areas, considerable pollution of streams is caused by drainage and washing liquors from farms or factories adopting mechanical methods of removing peas from pea vines. The drainage can be very grossly polluting owing to the high content of vegetable matter and the B.O.D. can be as much as 12,000 p.p.m. Since the drainage is comparatively small in volume and the trade is a seasonal one (about six weeks during the summer), biological methods of purification are not practicable, and the only feasible method is land treatment where local circumstances permit.

SEEPAGE FROM SILOS

According to Jones and Murdoch, a certain amount of stream pollution has been caused in this country in recent years by effluents from silage made from grass and other fodder crops; effluents from brick tower silos protected from the weather can be as much as 220 times as strong, judged by the B.O.D. test, as an average settled domestic sewage. Discharging the effluent on to neighbouring land would appear to be the only reasonable method of disposal.
CAUSES OF RIVER POLLUTION

DRAINAGE FROM FARMS AND MANURED LAND

During wet weather, drainage from farms and manured land may be washed into a river. Although some pollution may be caused in this way, it is unlikely at well-managed farms to be at all considerable, also the flow of the stream should be much above normal.

SURFACE DRAINAGE

Whilst discharges to foul water sewers pass to the sewage disposal works for treatment, those proceeding to surface water sewers may go straight to a stream. Pollution is liable to occur in this way from garages, trade premises, etc., situated close to the river, and can be due to

(a) harmful liquors, oil, etc., spilled accidentally on the ground (for example by leakages or bursting of barrels, pipes, tanks, and so forth) as well as floor washings; and

(b) careless discharges of polluting materials.

In some cases, discharges are sent down surface drains in the mistaken belief that these drain to the foul sewers.

ROAD DRAINAGE

This may contain toxic substances derived from the tar used for spraying the road surface. Experiments by Adam and his co-workers showed that phenols and tar bases (especially acridine) washed from the tar were highly toxic to golden carp. The British Road Tar Association has developed a special tar ("Brotox"), the washings from which are not toxic to fish, but it is more expensive than the ordinary toxic tars.

SLUDGE FROM MILL DAMS

In many parts of the country, particularly in Lancashire, Cheshire and Yorkshire, mill owners use large volumes of river water for process work and other purposes and in consequence have found it necessary to construct dams or reservoirs in or near the bed of the stream. Periodically, these mill dams become silted up with solid material derived from matter in suspension in the river water. It then becomes necessary to remove the accumulated deposits and to the mill owner a convenient way of doing this is to discharge them to the stream. Under Section 4 of the Rivers (Prevention of Pollution) Act, 1951, however, the sludging of mill dams in this way is an offence if carried out without the consent of a river board, but obviously the board would insist that the sludging be carried out by other methods (e.g. tipping the sludge on to waste ground) if at all practicable.
ASPECTS OF RIVER POLLUTION

BOILER BLOW-OFF WATER

This occasional discharge from boilers using alkaline conditioning agents is alkaline to phenolphthalein and has a high content of suspended solids. Since the volume is small, the pollution caused is usually negligible and is only likely to be serious in a fishing stream or where the dilution is low.

SHEEP WASHING

The washing of sheep in a small stream can cause pollution due to grease, dirt and chemicals, which may lead to mortality amongst fish. The washing should never be done in a river used for drinking purposes.

SHEEP DIPPING

This is a process carried out in order to control various parasites which infest sheep, and may have to be repeated several times a year. The sheep are fully immersed (generally in a large wooden tub) in a fluid containing a toxic chemical preparation (e.g. arsenious acid, arsenic-sulphur compounds, phenolic preparations, lime-sulphur dips, synthetic insecticides). The liquids are highly poisonous and grossly polluting, and should be disposed of on land far away from a stream as they may do extensive damage to fisheries. The Ministry of Agriculture and Fisheries suggest the disposal of the spent liquors in a trench or pit previously sprinkled with lime.

In recent years, the synthetic insecticide BHC ('gamexane') has been found to be particularly effective against the sheep scab parasite and has the advantage over the older chemicals of requiring only a single dipping.

WATERING OF CATTLE

Pollution caused by excreta from cattle, sheep, etc., drinking stream water will, in general, be small, and is unlikely to be serious except in a very small watercourse or in a feeder stream to a reservoir of a water authority.

ACCIDENTAL POLLUTION

In recent times there has been a considerable increase in the road transport of potentially polluting liquids (e.g. sulphuric acid, carbon disulphide, tar, phenols, etc.) in tankers. In the event of an accident involving spillage, the possibility especially in rural areas of pollution of a neighbouring stream by liquid finding its way by surface drains or by direct access to the stream cannot be overlooked. The danger would be particularly great in fishing streams or in streams feeding reservoirs.
CAUSES OF RIVER POLLUTION

UNKNOWN DISCHARGES

In certain districts, considerable pollution can be caused by unknown trade effluents discharging continuously or intermittently into

(a) streams difficult of access because they are hemmed in for much of their length by buildings or industrial premises, thus making observation possible only at widely separated points, and

(b) inaccessible culverts passing through or under densely populated or industrialized areas.

It is often very difficult to trace the source of such pollutions especially if the outlets are submerged and if the stream is already polluted. In the case of culverted streams, some indication of the presence of these discharges can sometimes be obtained if the discharge is highly coloured, or, in the cases of strong effluents or liquors containing some characteristic easily-detectable constituent (e.g. copper, cyanides, phenols) by sampling the stream above and below the culvert provided local circumstances permit.

The elimination of many of these pollutions is by no means easy. Some of the discharges, being of short duration, may be very difficult to trace and may occur during the night, at week-ends, or during holiday periods when it is known that a river inspector is not on duty. Often a complaint by a member of the public, or an examination of fish that have died as a result of the pollution, or the prompt taking and analysis of samples, may assist in solving the problem and reveal the source of the pollution. Obviously, a pollution officer cannot always be at the right spot if he has many miles of river to inspect but surprise visits at abnormal hours often bring quite astonishing and revealing things to light.

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CHAPTER 5

USES OF RIVER WATER

The fundamental importance of water for life on the earth needs little justification. Indeed, modern industrial developments would scarcely be possible without an adequate supply of water of the right degree of purity. It would be difficult to find a better illustration of the close connection between water usage and modern civilization than in the astronomical figures given in an American report\(^2\) for the estimated total water consumption in the U.S.A., namely about 100,000-150,000 million U.S. gallons\(^*\) per day. Of this tremendous total, about 25,000 million U.S. gallons per day are used by American industry. In smaller countries, such as Great Britain, water consumption is, of course, much below these figures. Southgate\(^3\) gives the total volume of water supplied by public water undertakings in Great Britain as approximately 1,000-1,500 million imperial gallons per day, but at the present time the figure would be even higher, probably over 2,000 million gallons.

According to Fox\(^4\), the average consumption of water taken over the whole world for drinking, washing and domestic uses is about 10-15 gallons per person per day. In some industrial cities, especially in the U.S.A., the per capita daily water consumption may be as much as 100 gallons or more, whilst in backward, rural, or desert areas, where piped water supplies and the water carriage system of sanitation are in most cases non-existent, the figure may be as low as 5 gallons. In Great Britain, water consumption in industrial towns may be as much as 40-50 gallons per head per day, and is tending to increase.

It is obviously of primary importance that water should be available to mankind in sufficient quantity. But scarcely of less significance is the quality of the water. It is in this connection that the pollution of many of our rivers looms as a problem of the first

* The U.S. gallon is about five-sixths of the imperial gallon.
magnitude and represents a wasteful misuse of water, for, in view of
the rising consumption of water and of the diminishing amounts
available from underground sources owing to demand exceeding
supply, more use will undoubtedly have to be made in the future of
rivers—even polluted reaches of rivers—as sources of supply for
drinking purposes. Conservation of the water resources of the area
in the exercise of the functions of a river board is a duty of the board
under Section 9 of the River Boards Act, 1948.

In this chapter, we shall consider the various uses of river water,
the requirements and qualities necessary for the particular purpose
or purposes for which the water is required, and the methods avail­
able to attain these requirements. The main uses of river water
to be considered can be grouped under the following headings:
(1) drinking purposes, (2) industry, (3) agriculture, (4) fisheries,
(5) navigation, and (6) recreation, including bathing and boating.
The particular use to which a river is put or may be put in the future
must be considered when fixing by-laws under the Rivers (Preven­
tion of Pollution) Act, 1951, prescribing standards of purity for
effluents discharging to the river.

For a more detailed consideration of water quality criteria and
for a critical evaluation of the literature on the subject, the reader
is referred to the very comprehensive report published by the
California State Water Pollution Control Board.

USE OF RIVER WATER FOR DRINKING
PURPOSES

Water authorities supplying drinking-water for human consumption
are under a statutory obligation to supply a pure and wholesome
water. TAYLOR has defined a water as pure and wholesome if it
is free from visible suspended matter, colour, odour and taste, from
all objectionable bacteria indicative of the presence of disease­
producing organisms, and contains no dissolved matter of mineral
or organic origin which in quality or quantity would render it
dangerous to health, and will not dissolve substances injurious to
health.

Rivers are being used to an increasing extent as sources of drinking­
water and, particularly if polluted, may require quite elaborate
methods to render the water suitable for the purpose.

The following methods are generally used for the treatment of
water required for drinking purposes:

(1) Storage of raw water. This effects quite a marked purification
and reduces somewhat the bacterial content. It is an impor­
tant means of ensuring reduction or even elimination of patho­
genic bacteria of sewage origin.
USES OF RIVER WATER

(ii) Screening and straining. These processes remove coarse solid materials and also small particles of suspended matter.

(iii) Coagulation with chemicals. Aluminium sulphate, sodium aluminate, and ferrous sulphate ("copperas") are commonly used as flocculating agents to remove colour, fine particles of suspended matter, turbidity, etc. More recently, activated silica (prepared by partial neutralization of sodium silicate with acid, chlorine, or carbon dioxide, followed by ageing for a short time) has been used in conjunction with aluminium sulphate as a coagulation aid.

(iv) Sand filtration. Slow sand filters were formerly relied upon for complete treatment of water but with the advent of modern methods of sterilization rapid sand filters either of the pressure or gravity type and dealing with greatly increased volumes are now finding favour.

(v) Sterilization. Chlorine and chloramines are used to remove bacteria from water. Ozone and chlorine dioxide also find limited application as sterilizing agents and sometimes have the advantage over chlorine of removing in addition tastes and odours.

(vi) Aeration is used to remove iron and manganese as well as volatile gases such as hydrogen sulphide and carbon dioxide.

(vii) Activated carbon is sometimes used in quantities of the order of a few p.p.m. to remove tastes, odours, and occasionally colour.

(viii) Softening of hard waters when considered desirable is carried out either by the older lime-soda process, which usually reduces the hardness to about 20-40 p.p.m. (as CaCO₃); or, by the more modern methods using ion-exchangers (cf. Chapter 13, page 510) which can give water of zero hardness and can be used for the complete demineralization of water in special cases.

(ix)Nitifying filters (cf. Chapter 12, page 456) have occasionally been used in the treatment of very polluted river waters high in ammoniacal nitrogen in order to oxidize biologically ammonia to nitrate and thus prevent any subsequent interference with chlorination. A high content of ammonia in river water used as a source of domestic water supplies is undesirable because ammonia reacts with chlorine to produce chloramines which are much less active as bactericidal agents than chlorine. The destruction of ammonia by chlorine so as to leave a residual of free chlorine requires a ratio of nearly 10 parts of chlorine to 1 part of ammoniacal nitrogen and in the presence of much organic matter even more chlorine would be required.
ASPECTS OF RIVER POLLUTION

(x) Chemical treatment to reduce corrosiveness. A water which is capable of depositing a very thin protective film of calcium carbonate on the interior of metal pipes is regarded as non-corrosive. When waters are corrosive (i.e. do not deposit this thin protective film), it is necessary to add certain chemicals to control the corrosive tendency, for instance 'Calgon' (sodium hexametaphosphate).

Detailed consideration of these methods is beyond the scope of this book and the reader is referred to special books dealing with water treatment and purification. By the use of suitable combinations of methods, it is generally possible to produce a safe palatable water even from polluted rivers. For instance, as CREMER has pointed out, the River Lee, which is fairly heavily polluted at Luton, is able to contribute no less than 54,000,000 gallons of water a day to the resources of the Metropolitan Water Board—certainly a triumph of modern water purification techniques.

The Ministry of Health has recommended bacteriological standards for piped drinking-water supplies entering the distribution system. These standards, which are based upon the presumptive count of coliform bacilli and upon the Bact. coli I count, are shown in Table 20.

Table 20. Bacteriological standards for piped drinking-water supplies

<table>
<thead>
<tr>
<th>Class</th>
<th>Classification</th>
<th>Presumptive coliform count per 100 ml. (acid and gas formation in MacConkey broth)</th>
<th>Bact. coli I count per 100 ml.*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Excellent</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Satisfactory</td>
<td>1-3</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>Suspicious</td>
<td>4-10</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>Unsatisfactory</td>
<td>&gt; 10</td>
<td>0 or more</td>
</tr>
</tbody>
</table>

* The presence of Bact. coli I places the sample in Class 4.

Throughout the year, 50 per cent of the water samples should fall into Class 1; 80 per cent should not fall below Class 2; and the remainder should not fall below Class 3. Piped supplies that have been efficiently sterilized by chlorination should fall into Class 1, i.e. such waters should be free from coliform organisms in 100 ml.

No chemical standards of quality for drinking-water have been put forward officially in this country. In the U.S.A., however, where the quality of natural waters is much more variable, various physical and chemical standards (in addition to bacteriological standards) have been published from time to time, the latest revision adopted by the U.S. Public Health Service in 1946 being shown in Table 21; whilst it is emphasized that all filtered water supplies
USES OF RIVER WATER

should conform to the specified limits for turbidity and colour, in the case of unfiltered waters a little laxity is permissible after local circumstances have been taken into consideration. Freedom from taste or odour for both filtered and unfiltered waters is considered desirable but here again judgment and discretion must be observed after all local factors have been investigated.

Table 21. United States physical and chemical drinking-water standards
(By courtesy of the U.S. Public Health Service)

<table>
<thead>
<tr>
<th>Property or constituent</th>
<th>Maximum permitted or suggested limiting concentration p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turbidity (silica scale)</td>
<td>10</td>
</tr>
<tr>
<td>Colour (Hazen units)</td>
<td>20</td>
</tr>
<tr>
<td>Fluoride (expressed as F)</td>
<td>1.5</td>
</tr>
<tr>
<td>Lead</td>
<td>0.1</td>
</tr>
<tr>
<td>Arsenic</td>
<td>0.05</td>
</tr>
<tr>
<td>Selenium</td>
<td>0.05</td>
</tr>
<tr>
<td>Chromate (expressed as Cr)</td>
<td>0.05</td>
</tr>
<tr>
<td>Copper</td>
<td>3.0*</td>
</tr>
<tr>
<td>Iron and Manganese</td>
<td>0.3</td>
</tr>
<tr>
<td>Zinc</td>
<td>125*</td>
</tr>
<tr>
<td>Magnesium</td>
<td>125*</td>
</tr>
<tr>
<td>Chloride (expressed as Cl)</td>
<td>250*</td>
</tr>
<tr>
<td>Sulphate (expressed as SO₄)</td>
<td>250*</td>
</tr>
<tr>
<td>Potassium (expressed as K₂HPO₄)</td>
<td>0.001*</td>
</tr>
<tr>
<td>Total solids</td>
<td>500</td>
</tr>
</tbody>
</table>

Chemically treated waters
(i.e. lime softening, ion-exchange, or other chemical treatment)

Total alkalinity should not exceed hardness by more than 35 p.p.m.
(expressed as CaCO₃)

pH value. Not more than about 10.6 (25° C)

Normal carbonaceous alkalinity. Not more than 120 p.p.m.
(expressed as CaCO₃)

Radioactivity (pages 47-51) is a more recent hazard to which water supplies may be exposed. Wolman and Gorman state that in the U.S.A. there is not yet general agreement on the limits of radioactivity permissible in drinking-water, but proposed maximum permissible levels taken from their paper are shown in Table 22.
INDUSTRIAL USE OF RIVER WATER

River water is used in large quantities by industry for steam-raising (boiler feed water), cooling purposes, process work, and water power. Consequently, when a site is chosen for a new factory, much consideration should be given to the quality as well as to the quantity of the available water. Among the largest industrial users or consumers of water in the country are the chemical industry, oil refineries, paper mills, power stations, and atomic energy plants.

BOILER FEED WATER

In general, river water used for steam-raising requires some treatment for the following reasons:

(i) To avoid corrosion of the boiler plates and fittings. Corrosion may be due to the presence of acidic substances, dissolved gases (oxygen and carbon dioxide), calcium and magnesium chlorides and nitrates, and iron and aluminium sulphates. Dissolved corrosive gases may be removed by de-aeration.

(ii) To prevent the deposition of hard scale on the boiler plates. This condition is caused by the presence of such scale-forming substances as calcium and magnesium bicarbonates and sulphates, and silica. Taylor states that if the amounts of calcium or magnesium bicarbonates do not exceed 100 p.p.m., the precipitated carbonates are deposited as a sludge and not as a scale. Scale is harmful because it tends to hinder free interchange of heat, thus causing fuel wastage, and may also lead to serious local overheating of the boiler. Softening of the water is necessary to remove scale-forming substances.

(iii) To minimize as far as possible the condition known as 'priming' or 'foaming'. In this case, froth is produced in such large
quantities that bubbles are carried over into the steam pipes. The presence of finely divided suspended matter, mineral or organic, tends to aggravate this condition. Foam production is usually considerably lessened by softening the water. Foaming can be controlled by adding to the water small quantities of solid synthetic polyamides. In order to prevent too great a concentration of soluble salts, or an objectionable accumulation of sludge at the bottom of a boiler, it is customary to open the blow-off cock occasionally, a practice often referred to as 'blowing-off' or 'blowing-down' the boiler. According to Jackson, the opening of the cock to keep down soluble salts is only necessary once or twice a day, the water level being reduced by about 1-6 in.; in order to prevent undue sludge accumulation the cock should be opened several times a day for a few seconds. Many modern installations have automatic blow-off devices. It is customary to discharge the blow-off water, which may be alkaline to phenolphthalein and high in suspended matter, to a stream, but the volume is small and generally causes little pollution.

Table 23, taken from a paper by Benger, gives the permissible concentration of soluble solids in low, medium, and high pressure boilers.

<table>
<thead>
<tr>
<th>Boiler pressure</th>
<th>Permissible concentration of soluble solids p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low up to 100</td>
<td>5000</td>
</tr>
<tr>
<td>100-250 Medium</td>
<td>2000</td>
</tr>
<tr>
<td>250-500 Medium</td>
<td>1500</td>
</tr>
<tr>
<td>500-1000 Medium</td>
<td>1000</td>
</tr>
<tr>
<td>High over 1,000</td>
<td>500</td>
</tr>
</tbody>
</table>

Water for use in low pressure boilers can be softened satisfactorily by the well-known lime-soda process. De-ionization of the water can also be carried out by the use of synthetic ion-exchangers (cf. page 510). The introduction into the boiler of sodium carbonate or caustic soda and a little quebracho extract (which contains tannins) helps to prevent scale formation and to remove corrosive dissolved oxygen. Sodium sulphite is often added to remove the last traces of dissolved oxygen. At high boiler pressures, it is necessary not only to maintain a high alkalinity in the boiler (pH about 11-0) but also to use phosphates (e.g. Na₃PO₄ or Na₂HPO₄) to condition the water and precipitate all the calcium.
and magnesium as insoluble phosphate sludges. According to Taylor\(^7\), the total hardness in boiler feed water should not exceed 10 p.p.m. (expressed as CaCO\(_3\)) for pressures up to 500 lb./in.\(^2\) but for higher pressures the hardness should be zero.

Silica even in small quantities is a very objectionable constituent of water used in high pressure boilers since it tends to form a very hard scale in boilers, boiler tubes, and on turbine blades especially in the presence of calcium, magnesium, iron, and aluminium salts. LEAP\(^1\) has found that up to about 200 p.p.m. of silica in water can be removed by treatment with cast-iron shavings whereby an active hydrated iron oxide is formed which has a high absorptive capacity for silica. Gwown and his co-workers\(^7\) say that boiler feed water for use in high pressure boilers should not contain more than 0.2 p.p.m. of dissolved silica, though 1–5 p.p.m. is permissible at low pressures; reduction of the soluble silica content to a low level can be accomplished by means of highly basic synthetic anion exchange resins containing quaternary amine groups. A common method of removing silica from water involves the use of magnesium or of dolomitic lime in conjunction with the hot or cold lime-soda softening process\(^15\).

**COOLING WATER**

Cooling water is essential for many industrial processes and the quantities required are often very considerable. For instance, a large firm on the banks of the River Mersey engaged in the manufacture of chemicals from petroleum uses about 36 million gallons per day of river water for cooling purposes and the amounts required are likely to increase in the future. At electricity generating stations of the thermal type, where superheated steam drives the turbines and is condensed back again to water, enormous volumes of cooling water are needed in the condensers and the amounts will increase as new stations are brought into operation or existing stations are enlarged. Most of the water abstracted in this way is subsequently returned to the watercourse. Table 24, based on data kindly supplied by the Central Electricity Authority, gives some idea of the quantities of river water used at certain power stations in industrial south Lancashire and of the approximate number of units generated per day. Where the amount of river water is likely to be insufficient to meet the needs of the power station, 'cooling towers' are erected; the water leaving the condensers is cooled in these towers and recirculated, thus making the amount of water required only a fraction of that needed for a 'once through' system. A certain amount of water is lost in this way by evaporation. Owing to the fact that some stations make use of direct
USES OF RIVER WATER

cooling and others of cooling towers, it is not possible to give any general rule for equating the number of units generated with the maximum water abstraction.

Table 24. Quantities of water used for cooling purposes at some power stations in South Lancashire

(By courtesy of the General Electricity Authority)

<table>
<thead>
<tr>
<th>Station</th>
<th>Source of water abstracted</th>
<th>Approx. volume of water abstracted (gal. per working day)</th>
<th>Approx. units generated per day (kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bolton</td>
<td>R. Tonge</td>
<td>9,510,000</td>
<td>788,000</td>
</tr>
<tr>
<td>* Bury</td>
<td>R. Irwell</td>
<td>15,150,000</td>
<td>120,000</td>
</tr>
<tr>
<td>* Cranesley 'A'</td>
<td>R. Irwell</td>
<td>30,490,000</td>
<td>635,000</td>
</tr>
<tr>
<td>* Cranesley 'B'</td>
<td>R. Irwell</td>
<td>153,680,000</td>
<td>2,000,000</td>
</tr>
<tr>
<td>* Radcliffe</td>
<td>R. Irwell</td>
<td>27,500,000</td>
<td>219,000</td>
</tr>
<tr>
<td>† Barton</td>
<td>Manchester Ship Canal</td>
<td>100,000,000</td>
<td>1,660,000</td>
</tr>
<tr>
<td>† Trafford</td>
<td>Manchester Ship Canal</td>
<td>57,600,000</td>
<td>1,129,000</td>
</tr>
</tbody>
</table>

* Cooling towers used.
† Thermod cooling used.

Whilst it may be agreed that the most important requirements of cooling water are that a large volume should be available at a reasonable cost and at as low a temperature as possible, nevertheless the quality of the water cannot be altogether ignored. As Powell has pointed out, the usefulness of water for cooling purposes can be impaired if it contains slime-forming micro-organisms and if appreciable amounts of scale-forming constituents, suspended solids, dissolved corrosive gases, acids, oil, and organic matter are present.

The efficiency of condensers decreases considerably when the tubes become coated with solid material, oil, bacterial slimes, etc. Hence, the turbidity, hardness, and suspended solids content of the river water should be low. Chlorination is usually used to control growths of undesirable micro-organisms. The amount of chlorine required naturally depends upon the quality of the river water and sufficient should be applied to ensure a small residual in the water leaving the condensers. According to Pike, 5 p.p.m. of chlorine (applied for 10-15 minutes every 3 hours) is usually enough but highly polluted waters may require 10 p.p.m. or even more. The presence of ammonia in cooling water is not looked upon with favour by power stations since it results in a greater chlorine consumption owing to the chlorine reacting with ammonia to give chloramines which are less effective sterilizing agents than chlorine itself.
Each industry usually requires for its processes a water having certain desirable and distinctive qualities but in many cases it must be remembered that local factors are of considerable importance. For instance, the amount of space available for a water treatment plant, the amount, quality and extent of the pollution of the sources of water at the disposal of the particular industry, and the cost of the treatment all have an important bearing on the choice of treatment.

In general, it is desirable to give river water some treatment before it can be used for process work and the methods used are similar to those employed for drinking-water. In some cases, water for industrial processes is supplied to the firms by a local authority. For example, Warrington Corporation gives special treatment to the polluted River Mersey water to enable the water to be used by manufacturers; the preliminary treatment, described by Sherratt\textsuperscript{21}, involves coagulation with aluminium sulphate assisted by activated sodium silicate, which, especially during drought periods, improves the flocculation and settlement very considerably. This treatment is followed by filtration through rapid gravity filters and chlorination.

The purity requirements of water used for process work in particular industries varies considerably according to the nature of the industry. \textit{Table 25}, abridged from a publication of the American Water Works Association\textsuperscript{6}, gives an approximate idea of the desirable upper limits of various constituents in water used in a number of selected industries.

Some of the more important of these industries will now receive more detailed consideration, but for further particulars the reader is referred to the special works and articles on the subject\textsuperscript{5, 18, 22, 23}.

\textit{Water for paper making}

Furnas\textsuperscript{22} states that the production of 1 ton of finished paper requires the use of 10,000–400,000 U.S. gallons (corresponding to about 8,300–330,000 imperial gallons) of water. Although for coarse paper the quality of the water is not of great importance, for the better class papers the water should be free from iron, manganese, suspended solids, colour, turbidity and oily matter and should not contain an excessive amount of soluble solids.

A large firm of paper manufacturers situated at Stoneclough on the polluted River Irwell require a high quality process water for the manufacture of cigarette paper, and for this purpose make use of the activated silica method; treatment of the raw river water comprises sedimentation, flocculation with aluminium sulphate and activated silica, sand filtration and chlorination\textsuperscript{21, 24}.
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Table 25. Water quality tolerances for industrial processes6 (desirable upper limits).
(Abridged from 'Water quality and treatments', 1950, by courtesy of the American Water Works Association)

<table>
<thead>
<tr>
<th>Industry</th>
<th>Turbidity p.p.m.</th>
<th>Colour p.p.m.</th>
<th>Hardness p.p.m.</th>
<th>Alkalinity to methyl orange p.p.m.</th>
<th>pH</th>
<th>Total solids p.p.m.</th>
<th>Iron + manganese p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brewing:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Light</td>
<td>10</td>
<td>—</td>
<td>75</td>
<td>6.5-7.0</td>
<td>500</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Dark</td>
<td>10</td>
<td>—</td>
<td>150</td>
<td>7.0</td>
<td>1,000</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Carbonated †</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>beverage</td>
<td>2</td>
<td>10</td>
<td>50</td>
<td></td>
<td>850</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>Paper and pulp:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Groundwood</td>
<td>50</td>
<td>20</td>
<td>180</td>
<td></td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Kraft pulp</td>
<td>25</td>
<td>15</td>
<td>100</td>
<td></td>
<td>300</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Soda and sulphate</td>
<td>15</td>
<td>10</td>
<td>100</td>
<td></td>
<td>200</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Light paper</td>
<td>5</td>
<td>5</td>
<td>50</td>
<td></td>
<td>200</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>Tanning</td>
<td>20</td>
<td>10-100</td>
<td>50-135</td>
<td>8.0</td>
<td>0</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Textile:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>General</td>
<td>5</td>
<td>20</td>
<td>20</td>
<td></td>
<td></td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Dying</td>
<td>5</td>
<td>5-20</td>
<td>20</td>
<td></td>
<td>1</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Wood scouring</td>
<td>5</td>
<td>70</td>
<td>20</td>
<td></td>
<td>3</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Cotton hardtack</td>
<td>5</td>
<td>5</td>
<td>20</td>
<td></td>
<td></td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Viscose rayon:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Production</td>
<td>5</td>
<td>5</td>
<td>8</td>
<td>56</td>
<td>100</td>
<td>0.05</td>
<td></td>
</tr>
<tr>
<td>Manufacture</td>
<td>0.3</td>
<td>—</td>
<td>55</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

* Should conform to drinking-water standards. Sodium chloride should not exceed 275 p.p.m. Fluoride should not exceed 1 p.p.m. (pp.)
† Water should conform to drinking-water standards and should be clear, colourless, and free from bacterial contamination.

Water for textile industries

Water used for textile manufacture should be relatively free from colour, turbidity, iron, and manganese, and should be soft. The use of hard water may cause deposition of insoluble calcium and magnesium compounds on the fabrics and so interfere with the subsequent dyeing processes. Iron and manganese are particularly objectionable constituents on account of their staining properties. NORDELL18 suggests that iron should not exceed 0.1 p.p.m. and that manganese should not exceed 0.05 p.p.m. Iron and manganese present in inorganic combination can be removed from water by aeration—iron at pH 7.0 or above, and manganese at a pH greater than 9.0—but organically combined iron and manganese usually require chemical coagulation (e.g. with aluminium sulphate) for their removal18.

Colour is an undesirable quality of water used in textile processes and it can sometimes be much reduced by chlorination. Thus, WHITLOCK23 quotes an example of a textile mill in Switzerland
having a water supply which was highly coloured owing to the presence of peaty matter. Treatment with 8 p.p.m. of chlorine reduced the colour from 70 to 15 Hazen units, giving a water which was satisfactory for use without any further treatment.

Table 26, taken from a paper by Benoit 24, gives the characteristics of good process water for the textile industries.

<table>
<thead>
<tr>
<th>Property</th>
<th>Desirable amount or value</th>
<th>Proposed corrective treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended solids</td>
<td>less than 5 p.p.m.</td>
<td>Fine screens; sand filter</td>
</tr>
<tr>
<td>Colour</td>
<td>0</td>
<td>Chemical flocculation, sedimentation and filtration</td>
</tr>
<tr>
<td>Hardness</td>
<td>less than 20 p.p.m. (as CaCO₃)</td>
<td>Softening (e.g. lime-soda, ion-exchange)</td>
</tr>
<tr>
<td>Iron</td>
<td>less than 0·2-0·5 p.p.m.</td>
<td>Arsenation and filtration; zeolite solvent</td>
</tr>
<tr>
<td>pH</td>
<td>about 7·0</td>
<td>Neutralization</td>
</tr>
</tbody>
</table>

Water used for dyeing and bleaching textiles should be free from colour, turbidity and suspended matter and should be soft and have a low content of organic matter. Freedom from iron and manganese is necessary to avoid the formation of unwanted colours 22. In general, the presence of calcium and magnesium is detrimental to dyeing with synthetic aniline dyestuffs 22 as sticky precipitates are formed resulting in uneven dyeing and poor shades.

Water for tanning

Water used in liming the hides for the purpose of loosening the hair roots should be low in free carbon dioxide and in bicarbonates otherwise a precipitate of calcium carbonate forms on the hide and interferes with the subsequent tanning process 22. Iron and manganese are particularly objectionable constituents in water used for tanning since they form dark-coloured tannates. According to Nordell 18, iron and manganese together should not be present in amounts greater than 0·1 p.p.m. Organic matter should not be present on account of its tendency to cause rotting or decay of the leather 22.

Water for food industries

Water for food industries should be clear, colourless, free from iron and manganese and from objectionable tastes and odours. It is necessary that the water should be of good bacteriological quality and desirable that the hardness should be low. Ozone can, with
advantage, be used for the sterilization of the water, whereas chlorination might produce undesirable tastes.

Water for laundries
Water for laundries should be free from colour, turbidity, aluminium, iron, and manganese, and should be soft so as to avoid wastage of soap and the formation of a white scum of calcium and magnesium soaps. Where the water is hard much can be done to improve the efficiency of the washing processes by the judicious use of synthetic detergents.

Water for pharmaceutical and biological preparations
Water for these products (drugs, serums, antitoxins) must be of an even higher degree of purity than drinking-water since they are administered in many cases by intravenous or intramuscular injection. In addition to the conventional water treatments (e.g. clarification, demineralization by ion-exchange, and sterilization), the water is further subjected to triple distillation at a temperature of over 283°C in order to remove "pyrogens"—complex agents of unknown character which, when they enter the blood stream, cause rise in temperature and fever.

POWER
Cheap power is still obtained at many textile and other mills by the old method of harnessing the natural energy of moving river water to drive a water-wheel or hydraulic turbine.

This principle finds modern application on a regional scale at the vast hydro-electric power stations set up in various parts of the world, especially where a high head of water (e.g. a waterfall) is available. An outstanding example of the utilization of rivers as sources of hydro-electric power is provided by the Tennessee river and its tributaries in the U.S.A. Here storage dams and hydro-electric power plants have been constructed by the Tennessee Valley Authority at various strategic points and the power production in 1944 was about 12,000 million kilowatt hours or about 2,700 kilowatt hours per person per annum. The scheme is a multiple purpose one involving not only the use of water for power, irrigation, navigation, and domestic supplies but also such projects as afforestation, flood prevention, and provision of natural parks. In cases where suitable falls occur on a river, as at Niagara Falls and the Victoria Falls, there is no need to provide expensive storage dams.

In Europe, Switzerland and Norway are foremost in utilizing rivers as cheap sources of hydro-electric power.

In Great Britain, the only important example of the use of
hydro-electric power is the Lochaber Water Power Scheme which supplies power for the works of the British Aluminium Co. at Fort William, Scotland.

Agricultural Uses of River Water

WATERING OF CATTLE AND OTHER LIVESTOCK

Although the drinking-water used for human consumption by most civilized countries is of a high standard of quality, much less attention is usually given to the sanitary quality of streams used for watering cattle and other domestic animals. According to Schroepfer, cattle drinking polluted waters can contract anthrax and bovine tuberculosis and the presence of pathogenic bacteria in the water in which cattle wade can lead easily to the contamination of the milk. Gill quotes a case of cattle becoming infected with tuberculosis as a result of drinking polluted stream water. Nevertheless, most experimental work on the drinking of sewage-contaminated water by cattle has shown that the animals were not adversely affected either in health or in condition. Thus, experiments by the Royal Veterinary College, London, in which cattle drank water containing sewage for 21 months, showed no evidence of harmful effects, and the conclusion was reached that "no such condition as sewage poisoning exists". Again, in an experiment in the U.S.A. in which pigs were given sewage, sewage effluents and sewage sludge over a period of 6 months and cows and steers were given sewage effluents, no untoward effects were observed and all the animals remained healthy. Robinson has concluded from experience in South Africa that the consumption of water containing human sewage was not injurious to cattle and, indeed, that they seem to prefer drinking sewage effluent rather than fresh water. Christiansen and Jepsen report that cows drinking brook water polluted by waste waters from a slaughterhouse remained free from tuberculosis despite the fact that 8 of the 15 samples taken from the brook contained B. tuberculosis. It does, therefore, seem reasonable to conclude from the available evidence that the drinking of stream water containing sewage does not appear to be injurious to cattle, at least in temperate climates.

Excessive salt concentrations in drinking-water can be harmful to animals. For example, Frant has shown that whilst brackish water containing up to 1 per cent of sodium chloride was suitable for cows, the animals showed signs of poisoning (loss of appetite, decreased milk production) when the sodium chloride content was increased to 1.5 per cent.

Cases are on record of domestic animals being poisoned or killed.
USES OF RIVER WATER

by drinking water containing blooms of certain blue-green algae. Death of the animals appears to be caused by some toxic substance produced by the algae.

WATER FOR IRRIGATION

The use of river water and of sewage effluents for irrigation is of special importance in arid districts in tropical and semi-tropical countries. The quality requirements of water used for irrigation have been discussed by Wilcox. Important characteristics of the water are the total concentration of soluble solids, the percentage of sodium (defined as $Na + Mg + Ca + K$), and the concentration of boron; permissible limits for these, quoted by Wilcox and based on a report by Schofield, are shown in Table 27.

Table 27. Permissible limits for soluble solids, sodium, and boron in irrigation water

<table>
<thead>
<tr>
<th>Class of water</th>
<th>Soluble solids p.p.m.</th>
<th>Sodium per cent</th>
<th>Boron p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sensitive crop*</td>
</tr>
<tr>
<td>Excellent</td>
<td>&lt; 175</td>
<td>&lt; 20</td>
<td>&lt; 0.33</td>
</tr>
<tr>
<td>Good</td>
<td>175-525</td>
<td>20-40</td>
<td>0.33-0.67</td>
</tr>
<tr>
<td>Permissible</td>
<td>525-1,400</td>
<td>40-60</td>
<td>0.67-1.00</td>
</tr>
<tr>
<td>Doubtful</td>
<td>1,400-2,100</td>
<td>60-80</td>
<td>1.00-1.25</td>
</tr>
<tr>
<td>Unsuitable</td>
<td>&gt; 2100</td>
<td>&gt; 80</td>
<td>&gt; 1.25</td>
</tr>
</tbody>
</table>

* Examples: fruit trees and bushes.
† Examples: tomato, wheat, barley, olive, pea, potato.
‡ Examples: carrots, lettuce, cabbage, turnip, onion, sugar-beet.

Boron, although apparently essential for plant growth in minute amounts, is toxic when its concentration reaches a figure of the order of 0.5-1.0 p.p.m., but as the table shows, plants vary somewhat in their tolerance to boron. Wilcox quotes a curious case of a stream in northern California (Cache Creek) which has a high boron content (1.78 p.p.m.) and is injurious to boron-sensitive plants but satisfactory for the more tolerant crops.

Sodium in excessive amounts in irrigation water causes the soil to become alkaline due to formation of sodium carbonate which, even in low concentrations, is harmful to plant life. Water of high pH value (above 9.0) and water containing more than traces of certain toxic metallic ions (e.g. lead, copper, cobalt, mercury, zinc, chromium, nickel, selenium, molybdenum) may be injurious to plants. * Concentrations in equivalents per million
In rural areas where water may be used for irrigation and for arsenical plant sprays, the U.S. Public Health Service has suggested that the chemical requirements and recommendations contained in their Drinking Water Standards (given on page 99) should be followed and that, in addition, the water should not contain more than 1.0 p.p.m. of boron or more than 1.0 p.p.m. of vanadium. It should be added that, so far as the author is aware, the presence of boron and vanadium, as well as of certain toxic substances (e.g., selenium) listed in the U.S. Public Health Service Drinking Water Standards, is unlikely in Great Britain unless it is the result of a trade waste discharge.

In many cases, for instance the growing of watercress, the water must be of satisfactory bacteriological quality since many examples of enteric infections have been traced to the use of sewage-polluted river water for watercress beds. Where there is any doubt about the quality of the water the watercress should be disinfected with a solution of sodium hypochlorite.

Wilcox has stressed that factors other than the chemical composition of the water play an important part in irrigation, for instance, the permeability of the soil, the method of irrigation used, the rainfall, the climate, soil management practices, and the species of crop.

**FISHERIES**

It is common knowledge that water satisfactory for industrial purposes or for navigation does not necessarily support fish life. Again, water unsafe for drinking purposes owing to bacterial contamination might yet be suitable for the support of fish. The investigations of Ellis and others (see also Chapter 7) have done much to indicate the conditions on the one hand suitable for, and on the other hand inimical to, the maintenance of fish life in streams. Various species of fish, and even individual fishes, showed marked differences in their degree of resistance or tolerance to external influences, and so conditions which may be satisfactory for coarse fish will not necessarily ensure the survival of game fish. Since quite short periods of adverse conditions can easily prove fatal to fish, it is emphasized by Ellis that high standards must be maintained even during summer conditions of high temperature and low flow and under maximum conditions of pollution. The main requirements desirable for the maintenance of good fish fauna in inland streams can be summarized as follows:

**Dissolved oxygen**—Ellis has given the minimum dissolved oxygen content of water for maintaining fish in healthy condition as 5 p.p.m. at 20° C, or about 57 per cent of saturation, and other
authors give figures of the same order of magnitude. *Game fish* (e.g. salmon and trout) require more dissolved oxygen than do *coarse* fish. Anything tending to reduce the amount of dissolved oxygen (e.g. organic pollution), or anything excluding atmospheric oxygen and so preventing re-aeration, such as oil (Chapter 3, page 24) or even ice, may, therefore, be harmful to fish. Indeed, Pentelow states that in the U.S.A., where freezing of rivers can occur in the winter, the layer of ice effectively prevents re-aeration of the stream water and quite commonly leads to mortality of fish during the winter even in clean waters—a very rare occurrence in this country.

**Temperature**—The effect of temperature on fish has already been discussed in Chapter 3 (page 39). It is generally agreed that salmon, trout and other game fish thrive best in cool water (temperature about 13–19°C) and they are less numerous at somewhat higher temperatures (19–22°C) whilst at water temperatures above about 23°C they are rarely or never observed. *Coarse* fish are able to withstand much higher temperatures.

**pH range**—Acidic or alkaline conditions in a stream are harmful to fish. Roberts, Grindley and Williams (see Chapter 3, Reference 16) state that freshwater fish usually thrive in waters having a pH value between 5·0 and 8·5 but Ellis considers the desirable pH range for the maintenance of fish life to be 6·7–8·6. It has been pointed out in a report of an American committee that many poorly dissociated acids and bases (e.g. ammonia) can be toxic quite apart from any effect they may have upon pH value, and consequently should not be judged merely upon the basis of pH but also by their own toxicity as determined by bio-assay methods.

A good reserve of natural bicarbonate alkalinity is desirable in a river in order to safeguard the river and prevent any sudden discharges of acid or alkali from causing any marked fall or rise in pH (see Chapter 10, page 396).

**Free carbon dioxide**—Free carbon dioxide in any considerable amount is lethal to fish and to their eggs. Ellis considers that the concentration of free carbon dioxide should not exceed 3 ml/l. (about 6 p.p.m.) and that any higher value usually indicates pollution. Free carbon dioxide might be produced by the oxidation of organic matter or by the action of acid discharges on bicarbonates.

**Ammonia**—Unpolluted natural waters have a very low content of ammonia but pollution by sewage and other nitrogenous organic wastes and by many chemical waste waters can increase the ammonia content to dangerous levels. Ellis considers that ammonia should not exceed about 2·5 p.p.m. It has been shown, however, that pH has a marked influence on the toxicity of
ammonia to fish and that the concentration of unionized ammonia, rather than total ammonia, is the important factor (see Chapter 7, page 168, and Chapter 10, page 372).

Freedom from toxic substances—A river water can have a satisfactory pH range and a high concentration of dissolved oxygen, and yet be unsuitable for the maintenance of fish owing to the presence of one or more substances toxic to fish. Ellis, therefore, has rightly stressed the importance of showing that specifically toxic substances are absent from a fishing stream.

The toxic effects of many inorganic and organic compounds have already been briefly discussed (see Chapter 3, pages 29 and 32), but a fuller discussion will be given later (see Chapter 7).

Dissolved salts—Brackish water is, in general, not favourable for the maintenance of freshwater fish and freshwater weeds (cf. Chapter 3, pages 34-35).

There is a relationship between electrical conductivity and the concentration of dissolved salts. Ellis states that the specific electrical conductance of most inland streams in the U.S.A. supporting fish life is between 150 and 500 mho (× 10⁻⁶) at 25°C and he suggests that in general this figure should not exceed 1,000 mho (× 10⁻⁶), or, for the more alkaline streams, should not be greater than 2,000 mho (× 10⁻⁶) at 25°C.

Freedom from excessive suspended matter—The effects of excessive suspended matter on fish have been discussed in Chapter 3, page 41.

It does not follow that even if all the requirements are satisfied, fish will necessarily be plentiful in a stream. Other factors may also influence the presence or absence of fish, for example the geological nature of the strata through which the river flows, the physical character of the stream and of the stream bed, the strength of the current, the relative abundance and nature of the plant life and the fish food present.

NAVIGATION

Many inland waterways in industrial areas are polluted but are still used for purposes of navigation. When one considers that the Manchester Ship Canal, which receives the whole of the pollution of the highly industrialized watershed of the Rivers Mersey, Irwell and their tributaries, has made Manchester one of the leading ports of the country, it is evident that the standards of water quality for a navigable waterway are by no means difficult of attainment!

Nevertheless, it is desirable that the water in canals and streams used for navigation should be reasonably free from the grosser forms of pollution. The most objectionable constituents are:

(a) alkali, which may cause damage to wooden structures;
USES OF RIVER WATER

(b) acid, which may cause corrosion to metal and concrete structures;

(c) excessive suspended matter which can lead to the formation of mud banks which hinder navigation and may have to be removed by dredging;

(d) hydrogen sulphide, which has an offensive smell and causes discoloration of paint and of copper and brass on boats, and corrosion of concrete structures.

Obviously, the water must not contain anything likely to affect prejudicially the health of those employed on vessels using the waterway.

RECREATIONAL USE

Water for recreational use (boating and bathing) should not only be free from colour, odour, or anything visible of an objectionable nature (such as sludge banks, suspended matter, floating material and oil) but also should not contain anything injurious to public health. Many rivers are polluted by sewage and may be unsuitable for bathing unless a bacteriological analysis has shown them to be reasonably safe. There is, however, no general agreement in this country on bacteriological standards of purity of bathing waters.*

In the case of swimming pools, as distinct from rivers, chlorination is practised to oxidize ammonia and organic matter and to maintain a small residual of free chlorine (0·2-0·5 p.p.m.) in order to protect bathers from the danger of bacterial and other infections.

In the U.S.A, a number of States have put forward standards for outdoor bathing waters based upon the B. coli count. For example, the Connecticut State Department of Health29 has proposed a classification of these waters which is given in Table 28.

Table 28. Connecticut State Department of Health: classification of outdoor bathing waters

<table>
<thead>
<tr>
<th>Class</th>
<th>Condition</th>
<th>Average B. coli count per 100 ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Good</td>
<td>0-50</td>
</tr>
<tr>
<td>B</td>
<td>Doubtful</td>
<td>51-300</td>
</tr>
<tr>
<td>C</td>
<td>Poor</td>
<td>501-1,000</td>
</tr>
<tr>
<td>D</td>
<td>Very poor</td>
<td>Over 1,000</td>
</tr>
</tbody>
</table>

The use of this classification is recommended by the Joint Committee on Bathing Places of the Conference of State Sanitary Engineers and the American Public Health Association29.

* Bacteriological standards have, however, now been recommended in a recent Ministry report.10
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17. Benger, M., 'Water supplies for oil refineries', Chem. & Ind. (Rec.), (1953) 170
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24 Hanson, C. G., 'Use of activated silica in water purification', Paper Tr., J., 131 (1950) No. 6, pp. 27, 28, 30, 32 and 34-7.


CHAPTER 6

BIOCHEMICAL AND PHYSICO-CHEMICAL ASPECTS OF RIVER POLLUTION

The ultimate aim of biochemistry is to gain complete insight into the winding series of changes which attend plant and animal metabolism.

EMIL FISCHER.

Faraday Lecture to the Chemical Society, 1907

A long stream course is a vast laboratory equipped for many processes. Into it it is carried every form of waste. Here through the seasons and the years nature ranges the changes in varied conditions, but always with the purpose that the experiment shall end with digestion of the raw products.

G. M. FAIR and M. C. WHIPPLE.
The Microscopy of Drinking Water, 1927

pH VALUE

The quantity of acid present in a solution as determined by titration is not necessarily related to the intensity of the acidity which, according to the ionic theory, depends upon the degree of electrolytic dissociation and therefore on the concentration of hydrogen ions. Owing to the very wide range of hydrogen ion concentrations, Sørensen suggested that a logarithmic scale would be more convenient to use in practice and he therefore introduced the term ‘pH’ to denote the intensity of the acidity or alkalinity of a solution and this was defined by the relationship:

\[ pH = -\log_{10} [H^+] \]

where \( [H^+] \) is the concentration of hydrogen ions (grammes per litre), so that \( [H^+] = 10^{-pH} \)

In view of the more modern concept of ionic activities, rather than ionic concentrations, developed by Lewis, Debye and Hückel, this relationship is now considered to be only an approximate one except in extremely dilute solutions. For most practical purposes, however, where an accuracy of \( \pm 0.1 \) unit is all that is required, this is of little consequence. The important thing is that the pH scale does provide a useful and convenient method of expressing varying intensities of acidity or alkalinity.
A precise definition of pH is given in a Standard published by the British Standards Institution in 1950; the difference in pH between two solutions is defined in terms of the E.M.F. of two cells containing these solutions, one of the solutions being the primary standard, a 0.05M solution of pure potassium hydrogen phthalate, whose pH value is defined as exactly 4.000 at 15°C.

It is often incorrectly stated that the range of pH values lies between 0 and 14. But as Cocking has pointed out, pH can be negative in very strongly acid solutions and can exceed 14 in highly alkaline solutions; the lowest known pH is minus 0.3 and the highest is 14.5.

Table 29 shows the pH scale and gives the relationship between pH value and hydrogen ion concentration at various values of the latter. Values intermediate between those given in the table can be obtained by calculation using the formula:

$$pH = -\log_{10} C_H = \frac{1}{\log_{10} C_H}$$

It is important to realize that the pH scale is a logarithmic one and not an arithmetical or linear scale. Thus, an increase in pH value by one unit means a tenfold decrease in hydrogen ion concentration (i.e., in the intensity of the acidity); for example, a solution of pH value 6.0 has ten times the hydrogen ion concentration of a solution having a pH of 7.0. Quite a small decrease or increase in pH is thus accompanied by a large variation in hydrogen ion concentration.
pH may mean a considerable rise or fall in hydrogen ion concentration. Each rise or fall in pH value by 0·1 means roughly a 20 per cent decrease or increase respectively in hydrogen ion concentration. Thus, a solution of pH 1·1 (0·08 g hydrogen ions per litre) has about 20 per cent less hydrogen ions than a solution of pH 1·0 (0·10 g hydrogen ions per litre). Again, since log10 2 = 0·3, if the pH falls by 0·3, the concentration of hydrogen ions is doubled.

Many important chemical and biochemical reactions only take place at a certain pH value or within a narrow pH range. Consequently the concept of pH is of great practical importance in industry, where, for the control of large-scale operations involving neutralization, chemical flocculation, etc., continuous pH recorders are available. The control of pH is particularly important in the chemical flocculation of trade wastes (Chapter 13, page 509) and in the anaerobic digestion of sewage sludges (Chapter 12, page 464) and of trade wastes (Chapter 13, page 519).

Rivers in Great Britain unpolluted by acid or alkaline wastes generally vary in pH value from about 5·0 (acid moorland peaty streams) to about 8·5 (chalk streams which are slightly alkaline to phenolphthalein indicator), but values outside these limits are sometimes encountered. The author once came across a river with a pH value of 8·9 and a phenolphthalein alkalinity of 5 p.p.m. (expressed as CaCO3); the stream was an excellent one easily supporting fish life. Intense photosynthesis can lead to alkaline conditions in a stream due to removal of carbon dioxide in sunlight by green plants (see page 396). Moorland streams are generally acid and soft, the acidity being due to organic acids (humic acid, acetic acid, etc.) derived from peat. Such streams are usually coloured yellowish or brownish. The author once encountered a stream with a pH value as low as 3·6 due to contamination with peat from the moors after heavy rain (for analysis, see Chapter 14, Table 101).

Solutions containing a weak acid and the salt of this acid with a strong base have the valuable property of altering in pH value only slightly on addition of a strong acid. A solution of a weak base and its salt with a strong acid behaves in a similar way on adding a strong base. This power of resistance to changes in acidity or alkalinity is called 'buffer action'. For instance, if a strong acid such as hydrochloric acid is added to a solution of sodium bicarbonate, neutral sodium chloride is formed and carbon dioxide is liberated:

\[
\text{NaHCO}_3 + \text{HCl} \rightarrow \text{NaCl} + \text{H}_2\text{O} + \text{CO}_2
\]

Since the strong hydrochloric acid is thereby replaced by a very weak acid, little change takes place in the pH value. The bicarbonate buffer system is of great importance in protecting
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streams from the harmful effects of acid discharges and in preventing wide fluctuations in pH value.

The majority of bacteria and other micro-organisms are killed by markedly acid or alkaline conditions and usually flourish best in a fairly neutral environment. In some cases the optimum pH range over which organisms grow covers very narrow limits. For example, the laboratory experiments of Heukelekian and Heinemann showed that in the case of bacteria producing methane anaerobically from certain organic compounds the optimum pH value for maximum growth was close to 7.0 and that on either side of neutrality the numbers of organisms developing fell very sharply. pH value, then, has a very marked effect upon the growth of bacteria. A practical illustration of this is reported by Morgan in connexion with the upper Ohio river, U.S.A., which receives acid mine drainage and much sewage pollution; the average count of coliform organisms was 160 and the maximum was 700 at times of low flow when the river water was acid, whereas at times of high flow when the acid was neutralized by the diluting water the count averaged 5,300 and reached a maximum of 37,000. An obvious disadvantage of the reduction in bacterial numbers caused by acidic conditions is a decrease in the rate at which a polluted stream undergoes self-purification.

Table 30 gives the limiting and optimum pH values for the growth of some typical micro-organisms. It will be seen from this table that, with the exception of the remarkable sulphur bacterium Thiobacillus thio-oxidans (see page 139), most bacteria are only able to grow down to a pH value of 4.0–5.0, whilst on the alkaline side the maximum pH value that can be tolerated by the majority of bacteria is about 9.0. The optimum pH value for good growth usually lies around neutrality, i.e. close to pH 7.0. Moulds are able to grow over a wider pH range and at rather lower pH values (i.e. more acidic conditions) than are most bacteria.

OXIDATION-REDUCTION POTENTIAL

The processes of oxidation and reduction play a fundamental part in chemical reactions. Formerly, oxidation was regarded as a process involving either addition of oxygen to a substance or the removal of hydrogen, whilst reduction involved the reverse process, namely the removal of oxygen or the addition of hydrogen. Typical examples are shown in the following equations:

\[
\text{Oxidation: } \quad \text{Addition of oxygen} \quad C + O_2 = CO_2 \\
\text{Removal of hydrogen} \quad H_2S = S + H_2
\]
Reduction

Removal of oxygen \[ 2\text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{O}_2 \]
Addition of hydrogen \[ \text{S} + \text{H}_2 = \text{H}_2\text{S} \]

Since many oxidations and reductions do not necessarily involve the participation of either oxygen or hydrogen, for instance the chlorination of ferrous salts with formation of ferric salts, some extension of the original ideas on oxidation and reduction is necessary so that elements other than oxygen and hydrogen can be included.

Table 30. pH ranges and optima for growth of various typical micro-organisms

<table>
<thead>
<tr>
<th>Organism</th>
<th>pH range for growth</th>
<th>Optimum pH value or range for growth</th>
<th>Reference (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Miscellaneous bacteria:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B. coli</td>
<td>4.4-7.8</td>
<td>6.5</td>
<td>7</td>
</tr>
<tr>
<td>B. pyocyanaum</td>
<td>5.6-8.0</td>
<td>6.8</td>
<td>7</td>
</tr>
<tr>
<td>B. subtilis</td>
<td>4.5-8.5</td>
<td>6.7</td>
<td>1</td>
</tr>
<tr>
<td>B. tuberculosis</td>
<td>4.5-8.0</td>
<td>6.0-6.5</td>
<td>1</td>
</tr>
<tr>
<td>B. dysenteriae</td>
<td>5.5-8.5</td>
<td>7.3</td>
<td>1</td>
</tr>
<tr>
<td>Vibrio cholerae</td>
<td>6.4-7.9</td>
<td>7.2</td>
<td>1</td>
</tr>
<tr>
<td>Streptococci</td>
<td>5.5-8.0</td>
<td>6.5</td>
<td>1</td>
</tr>
<tr>
<td>B. anthracis</td>
<td>6.0-8.5</td>
<td>7.2</td>
<td>1</td>
</tr>
<tr>
<td>Anaerobic bacteria</td>
<td>5.0-9.0</td>
<td>6.0-8.2</td>
<td>7</td>
</tr>
<tr>
<td>Nitrifying bacteria:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrosonomas</td>
<td>3.9-9.7</td>
<td>7.7-7.9</td>
<td>7</td>
</tr>
<tr>
<td>Nitrobacter</td>
<td>3.9-13.0</td>
<td>6.8-7.3</td>
<td>7</td>
</tr>
<tr>
<td>Azotobacter</td>
<td>3.6-9.2</td>
<td>6.5-7.8</td>
<td>7</td>
</tr>
<tr>
<td>Sulphur bacteria:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thiobacillus denitrificans</td>
<td>3.5-10.8</td>
<td>7.0-9.0</td>
<td>7</td>
</tr>
<tr>
<td>Thiobacillus thi-oxidans</td>
<td>1.0-6.0</td>
<td>2.0-4.0</td>
<td>7</td>
</tr>
<tr>
<td>Filamentous bacterium:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sphaerolithus natans</td>
<td>6.0-8.8</td>
<td>7.0-8.0</td>
<td>8</td>
</tr>
<tr>
<td>Moulds:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aspergillus niger</td>
<td></td>
<td>1.7-7.7</td>
<td>7</td>
</tr>
<tr>
<td>Fusarium redolens</td>
<td>3.0-10.0</td>
<td>5</td>
<td>1</td>
</tr>
<tr>
<td>Protozoa:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Paramecium</td>
<td>3.3-9.0</td>
<td>7.0-7.4</td>
<td>7</td>
</tr>
<tr>
<td>Colpidium</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to modern electronic ideas, oxidation involves the removal of one or more electrons and conversely reduction involves the addition of one or more electrons. Thus, in the oxidation of ferrous salts to ferric salts with chlorine in aqueous solution, there is a loss of one electron (\(\epsilon\)) whilst the reduction of ferric salts to ferrous salts with reducing agents, such as zinc in acid solution, involves the gain of one electron:

\[
\text{Oxidation} \quad \text{Fe}^{++} - \epsilon = \text{Fe}^{+++} \\
\text{Reduction} \quad \text{Fe}^{+++} + \epsilon = \text{Fe}^{++} 
\]
A substance is therefore an oxidizing agent or 'oxidant' when it can react with one or more electrons to produce a reducing agent or 'reductant':

\[ \text{Oxidant} + n\text{Reductant} \]

(\( n \) = number of electrons involved)

Every oxidation must involve the reduction of another chemical compound. Thus, in the preparation of water gas (a mixture of carbon monoxide and hydrogen) by passing water vapour (steam) over hot carbon (coke), the carbon is oxidized to carbon monoxide whilst the water is reduced to hydrogen:

\[ C + H_2O \rightarrow CO + H_2 \]

Oxidation processes of particular importance in connection with the biochemical reactions occurring in polluted streams are usually classified as

(i) *aerobic*—Here oxygen dissolved in the river water acts as the oxidizing agent; and

(ii) *anaerobic*—Here free or dissolved oxygen is not directly concerned but only oxygen combined in the form of some organic or inorganic compound. Common oxidizing agents acting in the absence of oxygen are nitrates and sulphates. In the latter case, evil-smelling hydrogen sulphide is produced.

The concept of oxidation-reduction potential, for many years of great value in analytical chemistry and biochemistry, has only within recent years assumed importance in connection with sewage treatment processes and pollution studies, possibly because of the difficulties involved in measuring oxidation-reduction potential and in obtaining reproducible results. Hood\(^1\) has defined oxidation-reduction potential (or 'redox potential') as 'the electrical pressure existing in a liquid as a result of the respective concentrations of oxidant and reductant present.'

If \( E_0 \) = the electrode potential in volts referred to the normal hydrogen electrode or half-cell, \( E_0 \) = a constant for the system, and \( n \) = number of electrons transferred, then the electrode potential at 20°C at constant pH value will be given by the well-known equation:

\[ E = E_0 + \frac{0.058}{n} \log \frac{[\text{Oxid.}]}{[\text{Red.}]} \]

where [Oxid.] and [Red.] are the concentrations of the oxidized and reduced forms of the substance under consideration. It will
be seen from this equation that the greater the proportion of oxidant present the higher (or more positive) the electrode potential will be, and, conversely, the greater the proportion of reductant present the lower (or the more negative) the potential will be. The significance of the constant \( E_0 \) can be seen by making \([\text{Oxid.}] = [\text{Red.}]\), when \( E_a = E_p \) and thus \( E_p \) is the electrode potential of the system, that is half oxidized and half reduced. Many workers have described the experimental procedures for determining oxidation-reduction potential and have given an account of the applications of these measurements for controlling biological processes at a sewage treatment plant. These applications include the detection of deposits, growths, etc., which might lead to septic conditions in sewers, the detection of toxic substances and industrial wastes, and the determination of conditions inside percolating filters, activated sludge aeration tanks and sludge digestion tanks. Positive \( E_a \) values are obtained under aerobic conditions existing in activated sludge plants, sand filters and low-rate percolating filters working normally. On the other hand, negative \( E_a \) values are obtained under anaerobic conditions such as, for example, in sludge digestion tanks, and in overloaded high-rate percolating filters. Hoorn and Rohlich state that a favourable \( E_a \) value for aerobic systems, such as activated sludge plants, is in the region of +200 to +600 mV; in sludge digestion plants, digestion is retarded unless the \( E_a \) value is maintained in the region of -100 to -200 mV. Hoocl refers to the case of an inefficient high-rate filter plant in which the filter lowered the oxidation-reduction potential from +311 mV to -39 mV; the final clarifier effluent had an even lower \( E_a \) value (-89 mV) and contained much hydrogen sulphide.

The study of oxidation-reduction potential in relation to river pollution is still in its infancy.

**BACTERIA**

Bacteria are minute living unicellular micro-organisms usually regarded as belonging to the vegetable kingdom, though they exhibit characteristics of both animals and plants. They are devoid of chlorophyll (the green colouring matter of plants) and with the exception of the small group of autotrophic bacteria (page 128) they are unable to synthesize materials such as proteins, fats, and carbohydrates required for their protoplasm from carbon dioxide, water and inorganic salts, but have to depend upon dead or living organic matter (see saprophytic and parasitic bacteria, page 127). Bacteria are widely distributed in Nature, being found in waters, soil, decaying organic matter, foods, animals and plants, in fact in any place where moisture and food are available.
majority of them move by means of one or more delicate thread-like organs called 'flagella'.

Morphologically, bacteria can be divided into four main groups14 according to their shape:

1. **cocci**: more or less spherical in shape
2. **bacilli**: rods
3. **spirilla**: spirally twisted forms or curved rods
4. **trichobacteria**: filamentous forms which may or may not be branched.

They are classified by the bacteriologist according to their morphological, biochemical and serological characteristics15. Bacteria generally reproduce by binary fission, that is divide to give two new organisms—hence the name 'Schizomycetes' (or 'fission fungi') by which they are also known (from Greek *schizèin*: to split or divide, and *mycètes*: fungi). The new cells go on growing and dividing at the same rate as the parent cells. The time taken for each fission (the generation time) can vary from days or hours down to as little as 20 minutes or even less, depending on the species and on external influences. As an illustration of the fantastically high rate of multiplication of bacteria, supposing that we start with one bacterium and we assume that fission takes place every 20 minutes, then the numbers of bacteria every 20 minutes up to 10 hours are shown in Table 31.

It will be seen from this table that a single bacterium (generation time = 20 minutes) can at the end of 1 hour produce theoretically 8 new bacteria, at the end of 2 hours 64 bacteria, at the end of 3 hours 32,768 bacteria, and at the end of 10 hours over 1,000,000,000 bacteria! More generally, the growth of bacteria takes place in accordance with the following exponential or logarithmic equation:

\[ n = n_0e^m \]

where

- \( n_0 \) = original numbers of bacteria
- \( n \) = numbers of bacteria at time \( t \)
- \( e \) = base of natural logarithms
- \( m \) = a constant.

When bacteria are transferred to a new environment, there is usually a delay (known as the 'lag phase') before they conform to the logarithmic phase growth demanded by the above equation.

It is fortunate that in practice the rate of multiplication of bacteria in polluted streams is limited by a variety of factors such as the amount and nature of the available food, temperature, the death of some of the bacteria (especially the older ones), the accumulation of toxic by-products, and the predatory activities of protozoa which feed upon bacteria. Multiplication of bacteria normally takes
place by fission but under certain circumstances can occur by means of small resistant reproductive bodies called 'spores'. Spores are particularly liable to form when the food supply of bacteria is becoming exhausted. These spores are more resistant to heat, desiccation, and other unfavourable external influences than are the vegetative cells. For instance, whilst spores can resist moist heat temperatures of 100°C or even higher, the vegetative forms are as a rule killed at much lower temperatures (usually 60–70°C). Hence, in bacteriological work sterilization of media and other liquids is usually effected by steam under pressure in a specially designed autoclave, i.e. 2 atm (or 15 lb./in.² gauge pressure) at about 122°C for about 30 minutes.

Most bacteria are extremely small and require the highest power of the optical microscope for their visual examination. According

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Bacterial numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 20</td>
<td>2</td>
</tr>
<tr>
<td>0 40</td>
<td>4</td>
</tr>
<tr>
<td>1 0</td>
<td>8</td>
</tr>
<tr>
<td>1 20</td>
<td>16</td>
</tr>
<tr>
<td>1 40</td>
<td>32</td>
</tr>
<tr>
<td>2 0</td>
<td>64</td>
</tr>
<tr>
<td>2 20</td>
<td>128</td>
</tr>
<tr>
<td>2 40</td>
<td>256</td>
</tr>
<tr>
<td>3 0</td>
<td>512</td>
</tr>
<tr>
<td>3 20</td>
<td>1,024</td>
</tr>
<tr>
<td>3 40</td>
<td>2,048</td>
</tr>
<tr>
<td>4 0</td>
<td>4,096</td>
</tr>
<tr>
<td>4 20</td>
<td>8,192</td>
</tr>
<tr>
<td>4 40</td>
<td>16,384</td>
</tr>
<tr>
<td>5 0</td>
<td>32,768</td>
</tr>
<tr>
<td>5 20</td>
<td>65,536</td>
</tr>
<tr>
<td>5 40</td>
<td>131,072</td>
</tr>
<tr>
<td>6 0</td>
<td>262,144</td>
</tr>
<tr>
<td>6 20</td>
<td>524,288</td>
</tr>
<tr>
<td>6 40</td>
<td>1,048,576</td>
</tr>
<tr>
<td>7 0</td>
<td>2,097,152</td>
</tr>
<tr>
<td>7 20</td>
<td>4,194,304</td>
</tr>
<tr>
<td>7 40</td>
<td>8,388,608</td>
</tr>
<tr>
<td>8 0</td>
<td>16,777,216</td>
</tr>
<tr>
<td>8 20</td>
<td>33,554,432</td>
</tr>
<tr>
<td>8 40</td>
<td>67,108,864</td>
</tr>
<tr>
<td>9 0</td>
<td>134,217,728</td>
</tr>
<tr>
<td>9 20</td>
<td>268,435,456</td>
</tr>
<tr>
<td>9 40</td>
<td>536,870,912</td>
</tr>
<tr>
<td>10 0</td>
<td>1,073,741,824</td>
</tr>
</tbody>
</table>
to Gainey and Lord, most cocci lie between the limits 0.5 μ and 1.5 μ, and most bacilli between 0.5 μ and 5 μ (μ = 1 micron = 0.001 mm = approximately 0.00004 in.). Many filamentous bacteria, however, are much larger and are visible to the naked eye.

Bacteria are much affected by external conditions such as light and other radiations, supersonic waves, temperature, pH (page 120), oxygen supply, chemical poisons, and the amount and nature of the food available. Minute traces of certain heavy metals in solution (especially silver, mercury, and copper), small amounts of chlorine, formaldehyde and phenols, and ultra-violet light have been found to be particularly efficacious in destroying bacteria. The studies of Chick have shown that when bacteria die in water on account of unfavourable conditions (e.g. presence of toxic substances), they do so in accordance with the exponential or logarithmic formula:

\[ \frac{N}{N_0} = e^{-kt} \]

or

\[ N = N_0 e^{-kt} \]

where

\[ N_0 = \text{initial numbers of bacteria} \]
\[ N = \text{numbers of bacteria after time } t \]
\[ e = \text{base of natural logarithms} \]
\[ k = \text{a constant} \]

It will be observed that this equation is analogous to that of a monomolecular chemical reaction, and also to the equation representing the rate of decay of radioactive elements.

The rate at which bacteria multiply decreases rapidly as the temperature falls and conversely increases as the temperature rises but with the majority of bacteria above about 45-55°C the rate decreases again until eventually at about 60-70°C most bacteria die.

Environmental conditions may have a marked effect not only on the shape and size of bacteria but also on the rate, course, and extent of the self-purification brought about in a stream by bacterial activity. When rivers are polluted by sewage, or by certain nitrogenous organic trade wastes (e.g. dairy wastes, slaughterhouse wastes, jiggery wastes, wastes from the manufacture of gelatine and size, etc.), the essential food requirements of bacteria are likely to be satisfied and rapid breakdown of organic matter takes place. Many carbonaceous trade wastes, however, are deficient in nitrogen and phosphorus (cf. page 518) and the rate of decomposition of the organic matter may in these cases be much reduced.

Among the most important bacteria found in river waters are natural water bacteria, soil bacteria (which increase in numbers...
after heavy rain or flooding), and bacteria of intestinal or sewage origin, some of which may be dangerous to health on account of the poisonous 'toxins' they secrete.

From the standpoint of river pollution, it is convenient to divide bacteria into contrasting groups based on such factors as temperature, ability to feed on dead or on living tissues, capacity to make use of organic or of inorganic materials, and power to utilize free or combined oxygen. These groups will now be discussed briefly.

**Cryophilic, Mesophilic and Thermophilic Bacteria**

Cryophilic (or Psychrophilic) bacteria thrive best at ordinary or somewhat lower temperatures, say about 12–20°C and are therefore of the greatest importance in connection with stream pollution.

Mesophilic bacteria work best in the temperature range 20–40°C with an optimum near 30°C. Although these are of lesser importance in stream pollution studies, it must be remembered that pathogenic bacteria of intestinal origin thrive best at the upper limit (i.e. about 37°C) of the mesophilic temperature range. Mesophilic bacteria are of great significance in connection with the anaerobic digestion of sewage sludge and certain trade wastes in heated tanks (see Chapter 12, page 464 and Chapter 13, page 519).

Thermophilic bacteria work best between 40°C and 60°C with an optimum at about 50°C and are mainly of interest in connection with experimental work on the thermophilic anaerobic digestion of sewage sludge. 19, 20, 21.

**Saprophytic and Parasitic Bacteria**

Most bacterial species are saprophytic bacteria, that is bacteria which feed upon dead organic matter (animal or vegetable) in soil or in water, breaking down complex organic material to simpler soluble chemical compounds which are used to build up bacterial protoplasm and also to furnish food for new plant life. Normal water bacteria are saprophytes playing an important part in the self-purification of rivers (see page 139) but not usually causing disease in man. There are very few materials of an organic nature which cannot be broken down by saprophytic bacteria. It has been shown, for example, that such unpromising and resistant materials as cellulose, lignin, rubber 22, paraffin wax 22, vaseline 23, benzene 23 and lubricating oils 24 can all be attacked and oxidized by certain bacteria.

Parasitic bacteria can only flourish for long periods by feeding upon a living creature (man, animal or plant) which acts, if unwillingly, as host. Many parasitic bacteria are also pathogenic, i.e. cause disease in living creatures, and since they may be present...
in sewage discharging to rivers, especially during epidemics, they may constitute a serious menace to public health. Fortunately, pathogens do not as a rule survive for very long outside the human body or other host. According to Taylor, in the case of river waters polluted by sewage containing typhoid bacteria, storage for about 5 days leads to a 99 per cent mortality of the bacteria and for 7 days a 99·9 per cent destruction. With very pure waters, however, several weeks' storage may be necessary to ensure the complete destruction of pathogenic bacteria.

**ASPECTS OF RIVER POLLUTION**

Autotrophic bacteria are a small group of bacteria which are remarkable because they use only simple substances for their food supply and obtain the carbon necessary for the synthesis of their carbohydrate, fat and protein from carbon dioxide, carbonates, or bicarbonates instead of from complex organic compounds. Since many of them derive their energy entirely by the oxidation of such inorganic substances as ammonia, sulphides and other sulphur compounds, hydrogen, and ferrous compounds, they are called chemosynthetic autotrophs. Typical examples of oxidation reactions brought about by chemosynthetic autotrophic bacteria are shown in Table 32.

**Table 32. Typical examples of oxidation reactions brought about by chemosynthetic autotrophic bacteria**

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Reaction</th>
<th>Organism responsible Type of bacteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>$2NH_3 + 3O_2 = 2HNO_2 + 2H_2O$</td>
<td>Nitrosomonas spp. Nitifying*</td>
</tr>
<tr>
<td>Nitrite</td>
<td>$2HNO_2 + O_2 = 2HNO_3$</td>
<td>Nitrobacter spp. Nitifying</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>$2H_2 + O_2 = 2H_2O$</td>
<td>Hydrogenomonas spp. Hydrogen oxidizing</td>
</tr>
<tr>
<td>Sulphide</td>
<td>$2H_2S + O_2 = 2S + 2H_2O$</td>
<td>Beggiatoa alba† Sulphur</td>
</tr>
<tr>
<td>Sulphur</td>
<td>$2S + 3O_2 + 2H_2O = 2H_2SO_4$</td>
<td>Thiobacillus thio-oxidans† Sulphur</td>
</tr>
<tr>
<td>Methane</td>
<td>$CH_4 + 2O_2 = CO_2 + 2H_2O$</td>
<td>Methanomonas Sulphur Methane-oxidizing</td>
</tr>
<tr>
<td>Ferrous salts</td>
<td>$4FeCO_3 + O_2 + 6H_2O \rightarrow 4Fe(OH)_3 + 4CO_2$</td>
<td>Gallionella† Iron</td>
</tr>
</tbody>
</table>

* Organisms converting ammonia to nitrites are sometimes called 'nitrifying'.
† Typical organisms. Other species can also bring about this reaction.
photosynthetic autotrophs. These contain a pigment related to the chlorophyll of plants and examples are the green and purple sulphur bacteria (page 139) which require the presence of compounds of sulphur to serve as inorganic substrate.

Heterotrophic bacteria in contrast to autotrophic bacteria are unable to synthesize their organic matter from carbon dioxide; they require organic compounds as sources of carbon as well as sources of energy and they utilize such substances as carbohydrates and amino-acids in addition to inorganic salts to build up their protoplasm. Most of the well-known bacteria (e.g. Bac. coli) belong to this class.

Some bacterial species (e.g. sulphate-reducing bacteria, page 137) can function both autotrophically and heterotrophically and for this reason many modern authors prefer to speak of an autotrophic or a heterotrophic 'way of life' 17.

**AEROBIC, ANAEROBIC AND FACULTATIVE BACTERIA**

Aerobic bacteria require the presence of free oxygen for their growth. Examples are bacteria in rivers bringing about self-purification, and bacteria in percolating filters and in activated sludge responsible for the purification of sewage.

Anaerobic bacteria will not as a rule develop in the presence of molecular oxygen but require combined oxygen. Examples are bacteria causing putrefaction of proteins (e.g. Clostridium sporogenes), sulphate-reducing bacteria (page 137) utilizing the combined oxygen in sulphates, and methane-producing bacteria which play so important a part in the anaerobic digestion of sewage sludge and of certain trade wastes. When the dissolved oxygen of a stream becomes exhausted owing to pollution by sewage or trade wastes, it is the anaerobic bacteria that are responsible for the resulting putrefaction of organic matter and the formation of hydrogen sulphide and other foul-smelling compounds.

Facultative bacteria will grow in the presence or absence of free oxygen. Examples are Streptococcus faecalis and other faecal streptococci.

The various chemical reactions brought about by bacteria are due to the activity of enzymes or 'ferments' elaborated by the bacterial cells. Enzymes are complex organic catalysts found in all plants and animals, and capable even in small quantities of initiating and accelerating specific chemical changes such as hydrolysis, oxidation, and reduction, in this way facilitating the conversion of complex insoluble substances into simpler soluble compounds. Enzymes differ from the purely inorganic catalysts in being thermostable, i.e. sensitive to, and eventually destroyed by, heat (especially
above 60-70°C). Their action is independent of the life processes of the cells from which they are secreted. Important factors influencing enzyme action are temperature (for which there is an optimum value for each enzyme), pH (which also shows an optimum for each enzyme) and toxic substances. Although many poisons (e.g. cyanides, fluorides and salts of heavy metals) destroy most enzymes, some substances ('activators') can increase the activity of enzymes (e.g. acids, i.e. hydrogen ions, can activate the enzyme pepsin). A few enzymes have been prepared in the crystalline state and resemble proteins in general properties but the majority of enzymes are colloidal in character. Enzymes may be extra-cellular (i.e. secreted outside the bacterial cell) or they may be intra-cellular (i.e. they may remain inside the cell). Bacteria are unable to utilize for their metabolism complex molecules (e.g. proteins and polysaccharides) which cannot pass through the cell wall. Extra-cellular enzymes play the important part of digesting and breaking down these large molecules into simpler compounds which can diffuse through the cell wall and so become readily available for bacterial growth and energy requirements.

Enzymes are generally specific in their action on a particular substance (the 'substrate') or group of related substances. This means that a bacterial cell must contain or elaborate a great variety of enzymes, in fact one for each reaction or process carried out. Most enzymes (except a few of the longest known ones, such as pepsin and trypsin) are named after the particular substance (or group of substances) upon which they act, with the addition of the suffix 'ase'. Among some of the more important types of bacterial enzymes are the following:

Esterases
These enzymes hydrolyse esters and fats to their component alcohol and fatty acid. For instance, the enzyme lipase converts fats into glycerol and fatty acids. Lipase has been found in activated sludge.

Carbohydrases
These effect the hydrolysis of complex carbohydrates to the relatively simple sugars. For instance, cellulase converts cellulose to cellobiose, amylase hydrolyses starch to maltose, cellobiase breaks down cellobiose to glucose, and maltase hydrolyses maltose to glucose. Amylase has been detected in activated sludge.

Proteases
These are protein-splitting or 'proteolytic' enzymes (e.g. trypsin)
having the power of hydrolysing the -CO-NH- linkage in proteins which are broken down to the simpler polypeptides and eventually to amino-acids. Proteases have been detected in activated sludge.  

Amidases

These are de-aminating enzymes which hydrolyse certain organic nitrogen compounds. An important example is the enzyme urease which converts urea to ammonia and carbon dioxide:

\[
\text{CO}_2(\text{NH}_2)_2 + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2\text{NH}_3
\]

Decarboxylases

These enzymes remove carbon dioxide from carboxylic acids or from amino-acids:

\[
\begin{align*}
\text{R'CO'COOH} & \rightarrow \text{R'CHO} + \text{CO}_2 \\
\text{R'CH(\text{NH}_2)} \cdot \text{COOH} & \rightarrow \text{R'CH}_2\text{NH}_2 + \text{CO}_2
\end{align*}
\]

Oxidizing enzymes

Oxidases (aerobic oxidases)—These enzymes oxidize reducing substances in the presence of oxygen and so play an important part in the biological purification of sewage and in the processes leading to self-purification in rivers. The experiments of Woolridge and Standfast appear to show that the most important factor in the biochemical oxidation of sewage by activated sludge is the presence of bacterial enzymes which bring about oxidation-reduction reactions. These enzymes may be associated either with living or dead cells but it is probable that the living cells are more active for certain oxidations. Ingols has discussed the functions of oxidation-reduction enzymes in activated sludge and suggests that the groups of enzymes which develop in the sludge are determined by the temperature, amount of oxygen supplied, and the types of food, as well as pH and the concentration of the enzymes, profoundly affect the activity of the sludge.

Dehydrogenases (anaerobic oxidases)—These enzymes bring about oxidations by the removal of hydrogen. This is effected by the activation of hydrogen in a compound (xH₂), and the transfer of the activated hydrogen to a hydrogen acceptor, A. (In a few cases, oxygen may act as a hydrogen acceptor.) Thus, the compound xH₂ is oxidized, and the substance A is reduced in accordance with the equation:

\[
x\text{H}_2 + A = x + A\text{H}_2
\]

For example, the blue dyestuff methylene blue, used as a stability indicator in work on sewage and polluted rivers (see page 377),
can act as a hydrogen acceptor in the manner just indicated, being reduced anaerobically to a colourless leuco compound in the presence of sewage or other reducing agent, and in the absence of oxygen or nitrate:

\[
\text{Methylene blue} \quad \text{Leuco-methylene blue}
\]

This reaction is reversible, free oxygen oxidizing the colourless leuco compound back to the blue dye.

Crude sewage contains many millions of bacteria but the numbers are very much reduced by the biological treatment of the sewage (e.g. by percolating filters or by the activated sludge process), and still further reduced by sand filtration or, better, chlorination. This is illustrated by the data given in Tables 33 and 34 which show that

(a) treatment of sewage by activated sludge gives a good reduction in bacterial numbers, generally greater than 90 per cent;
(b) chlorination reduces the numbers of bacteria in the final effluent to very low levels; and
(c) raw sewage contains fewer bacteria during the colder winter months than in the summer.

The numbers of bacteria in river water are naturally very variable and depend upon the degree of sewage pollution, the rate of self-purification, the weather, and many other factors. Data quoted by Barritt for the Illinois river, which is polluted by sewage from Chicago and other communities, show that the bacterial count for the 11 months October 1921 to August 1922 averaged 1,913,100 at a point 35 miles below Lake Michigan but this figure fell to only 13,486 at a point 362 miles below the lake.

Work carried out by the Water Pollution Research Laboratory has indicated that the numbers of bacteria in the River Avon and its tributaries increased considerably during wet weather; for instance in June 1945, bacterial counts were 2–4 times as great in the Finham Brook below a discharge of sewage effluent in wet weather than in dry weather. It was suggested that one factor responsible for the increase may be the operation of storm overflows and the discharge of storm water sewage during periods of heavy rain.
Since bacteria tend to attach themselves to suspended matter, large numbers are always found in the mud on the bed of a stream.

Table 33. Bacterial counts in raw sewage and treated effluent at Easterly Plant, Cleveland, Ohio. Average figures for year 1940

<table>
<thead>
<tr>
<th></th>
<th>20°C agar plate count numbers per ml.</th>
<th>Presumptive count of coliform organisms numbers per ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sewage</td>
<td>2,700,000</td>
<td>295,000</td>
</tr>
<tr>
<td>Activated sludge plant effluent. Unchlorinated</td>
<td>37,200</td>
<td>1,200</td>
</tr>
<tr>
<td>Activated sludge plant effluent. Chlorinated</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>Reduction in count. Unchlorinated</td>
<td>96-6%</td>
<td>99-6%</td>
</tr>
<tr>
<td>Reduction in count. Chlorinated</td>
<td>99-99%</td>
<td>99-99%</td>
</tr>
</tbody>
</table>

Table 34. Reduction in numbers of bacteria by activated sludge treatment of Manchester (Daiaphlume) sewage.

<table>
<thead>
<tr>
<th></th>
<th>Average agar plate count per ml. (18-5°C in 72 h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sewage (detritus free)</td>
<td>Raw sewage (detritus free)</td>
</tr>
<tr>
<td>Final activated sludge effluent</td>
<td>Final activated sludge effluent</td>
</tr>
<tr>
<td>Reduction in count.</td>
<td>Reduction in count.</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

CYCLES OF ORGANIC MATTER IN NATURE

The most important elements in organic compounds, namely carbon, nitrogen, and sulphur, undergo important cyclic changes in the soil, in streams, and during the various processes associated with the disposal and treatment of sewage. The organic compounds are broken down by bacteria to simpler compounds utilized as food for plants, which are able to re-convert them to organic compounds needed for their life processes. In view of their great importance, the three cycles involving carbon, nitrogen, and sulphur will be discussed in detail.

THE CARBON CYCLE

Organic carbonaceous matter in rivers, which may arise from dead and living animals and plants, from sewage and industrial wastes,
and from soil erosion, is oxidized by aerobic bacteria in the presence of dissolved oxygen to carbon dioxide, which may be neutralized in part by basic elements (sodium, calcium, magnesium, etc.) to bicarbonates or carbonates:

\[ \text{C}_\text{a} + \text{O}_2 \rightarrow \text{CO}_2 \]

In this way, 1 ton of carbon can give rise to over 8,000 lb. of carbon dioxide. This process is analogous to respiration in animals and plants whereby oxygen is taken in and carbon dioxide given off.

The reverse process (production of oxygen from carbon dioxide) is termed 'photosynthesis' and is carried out only by green plants containing chlorophyll (e.g. algae) in the presence of sunlight; it involves the formation of oxygen and the utilization of the carbon for the synthesis of complex organic compounds such as fats, carbohydrates, etc. Thus the formation of a relatively simple carbohydrate (a hexose sugar) can be represented as follows:

\[ 6\text{CO}_2 + 6\text{H}_2\text{O} \xrightarrow{\text{chlorophyll in presence of light}} \text{C}_6\text{H}_{12}\text{O}_6 + 6\text{O}_2 \]

This reaction is an endothermic one, the energy required being obtained from sunlight. It is probable that formaldehyde is formed as an intermediate product and then undergoes condensation to give sugars, starches, etc.,

\[ 6\text{CO}_2 \xrightarrow{\text{reduction}} 6\text{H} \cdot \text{CHO} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 \]

The reduction of carbon dioxide to formaldehyde has actually been carried out in the laboratory by Fenton by passing carbon dioxide into water containing sticks of magnesium metal. Photosynthesis is one of the most important of all biochemical reactions since it enables plant life to synthesize complicated organic compounds needed for plant growth from relatively simple substances and it is also one of the important natural forces helping to maintain the dissolved oxygen content of streams at a high level. Photosynthesis only takes place in the presence of bright light but, in the dark, plants continue to respire like animals, oxygen being taken up and carbon dioxide given off. For this reason, the dissolved oxygen content of a stream tends to fall at night.

In the absence of oxygen, anaerobic bacteria metabolize carbohydrates and other organic compounds and we have the well-known process of putrefaction leading to the reduction of carbon to methane. This occurs in sewage sludge digestion tanks, in septic tanks, during the anaerobic digestion of industrial wastes, and in sludge and mud deposits and decomposing vegetation at the
bottom of streams. In the case of cellulose, the reaction can be represented by the equation:
\[(C_6H_{10}O_5)_n + nH_2O = 3nCH_4 + 3nCO_2\]
cellulose methane

Anaerobic decomposition with formation of methane gas also takes place after a stream has been completely denuded of its dissolved oxygen and nitrate by heavy discharges of sewage or trade wastes. The bubbles of gas rising to the surface when stagnant backwaters, ponds, pools, and marshes are stirred or otherwise disturbed contain methane; hence the name 'marsh gas' formerly applied to methane. Roscoe and Schieler 38 record the interesting fact that the famous scientist Bunsen in 1848 collected gas from a pond in Marburg and the gas contained large quantities of methane produced by the bacterial decomposition of cellulose in the vegetable debris. Anaerobic decomposition of nitrogenous organic compounds containing sulphur also gives methane and carbon dioxide, and in addition organic acids, phenols, and ammonia as well as compounds having an objectionable odour, such as hydrogen sulphide, mercaptans, indole, skatole and organic amines.

THE NITROGEN CYCLE.
Decomposition of nitrogenous organic matter either by aerobic or anaerobic bacteria gives rise to ammonia. The oxidation of ammonia by aerobic bacteria, a process usually referred to as 'nitrification', produces first nitrates and then nitrates and two distinct groups of bacteria are concerned with these reactions:

(i) Bacteria which can only convert ammonia to nitrite, e.g. Nitrosococcus and Nitrosomonas:
\[2NH_3 + 3O_2 = 2HNO_2 + 2H_2O\]
These are often termed 'nitrosifying' bacteria.

(ii) Bacteria which can only oxidize nitrates to nitrates, e.g. Nitrobacter:
\[2HNO_2 + O_2 = 2HNO_3\]
It is now generally accepted that amongst the factors essential for nitrification are the presence of phosphates to supply nutrient material for the bacteria, the presence of oxygen, and the presence of a base or bases (e.g. sodium, calcium, etc.) to neutralize the nitrous and nitric acids. The presence of organic matter is not necessary; certain organic matter appears to have an inhibiting effect on nitrification. In the activated sludge process of sewage purification, for example, nitrification only commences when clarification of the sewage is almost complete and carbonaceous matter has been almost completely oxidized. Nitrifying bacteria are very susceptible to the action of toxic substances.
136 ASPECTS OF RIVER POLLUTION

Meiklejohn, very low concentrations of iron enhance the activity of nitrifying bacteria but manganese, even in low concentrations, is toxic to the bacteria. Nitrifying bacteria belong to the remarkable group (autotrophic bacteria, page 129) which derive their energy from the oxidation of simple inorganic materials.

Nitrates, the final oxidation product of ammonia, serve as food for plant life and is used by plants for the building up of plant proteins. The decay of proteins leads to the formation of ammonia, thus completing the nitrogen cycle.

The reduction of nitrates, or 'denitrification', can be brought about by certain nitrate-reducing bacteria especially in the presence of carbonaceous matter and of only limited amounts of oxygen. This happens, for instance, in heavily polluted streams, and in sewage percolating filters that have become 'ponded' or clogged (cf. Chapter 12, page 434). During denitrification, nitrates are reduced to nitrites and finally to ammonia, though under certain circumstances nitrous oxide (\(N_2O\)) and nitrogen are also produced.

Two other intermediate products of the biochemical oxidation and reduction of nitrogen compounds have been reported, namely hydroxylamine, \(NH_2OH\), and hyponitrous acid, \(H_2N_2O_2\):

Nitrification: \(NH_3\rightarrow NH_2OH\rightarrow H_2N_2O_2\rightarrow HNO_2\rightarrow HNO_3\)

Denitrification: \(HNO_3\rightarrow HNO_2\rightarrow H_2N_2O_2\rightarrow NH_2OH\rightarrow NH_3\)

As long ago as 1935, Corbet showed that oxidation of ammonium sulphate by cultures of soil micro-organisms gave hyponitrous acid as an intermediate compound. Recently, Tanaka has reported that during the autumn the dissolved oxygen content of the bottom layers of Lake Kizaki-Ko is greatly decreased, and this favours reduction of nitrate by nitrate-reducing bacteria and the formation of nitrite and hydroxylamine in the bottom layers.

THE SULPHUR CYCLE

When proteins containing sulphur (e.g. egg albumin) undergo anaerobic decomposition by bacteria (e.g. by \(E. coli\)) the foul-smelling gas hydrogen sulphide is produced due to reduction of cystine formed by hydrolysis of the protein:

\[
\begin{align*}
CH_2CH(NH_2)\cdot COOH  \\
\downarrow S  \\
CH_2CH(NH_2)\cdot COOH + 10H &\rightarrow 2H_2S + 2NH_3 + 2CH_3\cdot COOH
\end{align*}
\]

cystine
Small amounts of other malodorous sulphur compounds are also produced as by-products, for example methyl mercaptan (CH\(_3\)SH) and thioglycollic acid (CH\(_2\)SH·COOH). This reaction, which only occurs when a stream is devoid of both dissolved oxygen and nitrate, is objectionable not only on account of the odour nuisance but also because hydrogen sulphide blackens lead paint and causes corrosion to concrete structures. On the other hand, decomposition of proteins under aerobic conditions leads to the formation of sulphates which are odourless, and relatively harmless so long as oxygen and nitrates are present to prevent reduction to hydrogen sulphide.

The transformations which sulphur compounds undergo are in many respects analogous to those occurring with nitrogen compounds. Just as ammonia can be oxidized to nitrate which can be reduced back again to ammonia, so hydrogen sulphide can be oxidized to sulphate which in turn can be reduced back again to hydrogen sulphide to complete the sulphur cycle. The bacterial sulphur cycle is of great importance in connection with problems of river pollution and the treatment of sewage, and is shown diagrammatically in Figure 1. Brief reference will now be made to the more important bacteria bringing about these changes.

**SULPHATE-REDUCING BACTERIA**

The best known of these bacteria is *Desulphovibrio desulphuricans* which is of great importance since it produces hydrogen sulphide anaerobically from sulphates in the presence of a reducing agent which is usually organic matter:

\[ \text{H}_2\text{SO}_4 + 8\text{H} = \text{H}_2\text{S} + 4\text{H}_2\text{O} \]

The hydrogen required for this reaction is donated by the organic
matter which is oxidized to carbon dioxide. For example, the reduction of sodium sulphate in the presence of the organic compound acetic acid can be represented by the equation:

\[ \text{CH}_3\text{COOH} + \text{Na}_2\text{SO}_4 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{S} + \text{CO}_2 + \text{H}_2\text{O} \]

Conditions essential for this bacterial reduction are the absence of free oxygen and of nitrates, the presence of organic matter, and a fairly high temperature. These bacteria are, therefore, likely to be specially active in polluted rivers devoid of dissolved oxygen, particularly in the mud on the stream bed, during the summer months. Putrescent river mud containing sulphate-reducing organisms generally contains black ferrous sulphide, FeS, formed by interaction of hydrogen sulphide and ferrous compounds. Sulphate-reducing bacteria can also grow autotrophically in a purely inorganic medium provided that hydrogen is present as substrate.\(^47\)

Heukelien\(^48\) has found that sewage contains only a few sulphate-reducing bacteria (about 60-600 per ml) but much larger numbers occur in sewer growths and in sewage sludges. Apparently growth of these bacteria only takes place when the oxidation-reduction potential (page 120) of the sewage falls to a certain level.

These bacteria, as well as proteolytic bacteria decomposing organic sulphur compounds anaerobically, are responsible for the formation of hydrogen sulphide in sewers, which, especially in warm climates, can lead to severe corrosion of the concrete due to the bacterial oxidation of hydrogen sulphide eventually to sulphuric acid.\(^49,50\) The corrosion occurs at and above the water level and only takes place when air is present in the sewer. Chlorination of the sewage destroys hydrogen sulphide as well as inhibiting bacterial action, and appears to be the cheapest and simplest method of preventing or delaying corrosion.

**SULPHIDE-OXIDIZING BACTERIA**

The best known of these is *Beggiatoa* which belongs to the group of sulphur bacteria (*Thiobacteriales*). Several species of *Beggiatoa* exist all of which oxidize sulphides aerobically to free sulphur:

\[ 2\text{H}_2\text{S} + \text{O}_2 = 2\text{H}_2\text{O} + 2\text{S} \]

A common form, *Beggiatoa alba*, consists of colourless or greyish motile filaments containing sulphur granules, and is often found as a velvety covering on the bed of polluted streams.\(^*\)

Certain other sulphur bacteria, belonging to the class of photosynthetic autotrophs (cf. pages 128-9) are able to oxidize sulphide to sulphur anaerobically in the presence of sunlight, using carbon

\(^*\) This is one of the organisms present in "sewage fungus" (see page 224).
dioxide (e.g. bicarbonate) as sole source of carbon, and mineral nutrients (e.g. nitrogen, phosphorus, potassium and magnesium); the carbon dioxide here acts as an electron-acceptor (cf. page 131) and is reduced to formaldehyde which is used in the synthesis of more complex organic matter:

\[
\text{CO}_2 + 2\text{H}_2\text{S} \xrightarrow{\text{light}} \text{H} \cdot \text{CH} \cdot \text{O} + \text{H}_2\text{O} + 2\text{S}
\]

Examples are the purple sulphur bacterium *Chromatium* and the green sulphur bacterium *Chlorobium* which contain pigments allied to the plant chlorophylls. These bacteria, which may be present in putrescent organic matter, mud, stagnant pools and waters containing hydrogen sulphide, and in sewage, tend to impart intense colours to the waters in which they proliferate. Zobell suggests that so-called 'red water' or 'bloody seas' reported by various observers may be due to the presence of purple sulphur bacteria. *Chromatium* and some species of *Chlorobium* can carry the oxidation of sulphide still farther with formation of sulphate:

\[
2\text{CO}_2 + \text{H}_2\text{S} + 2\text{H}_2\text{O} \xrightarrow{\text{thio-oxidants}} 2\text{H} \cdot \text{CH} \cdot \text{O} + \text{H}_2\text{SO}_4
\]

**SULPHUR-OXIDIZING BACTERIA**

These bacteria oxidize sulphur to sulphate. *Chromatium* and some *Chlorobium* can carry out this reaction anaerobically in the presence of sunlight:

\[
2\text{S} + 3\text{CO}_2 + 5\text{H}_2\text{O} \xrightarrow{\text{thio-oxidants}} 3\text{H} \cdot \text{CH} \cdot \text{O} + 2\text{H}_2\text{SO}_4
\]

But the most important sulphur-oxidizing bacteria are those oxidizing sulphur to sulphuric acid aerobically, namely the *Thiobacilli*:

\[
2\text{S} + 2\text{H}_2\text{O} + 3\text{O}_2 = 2\text{H}_2\text{SO}_4
\]

*Thiobacillus thio-oxidans*, the most notable of the group, is one of the most interesting micro-organisms. It belongs to the class of autotrophic bacteria and utilizes free carbon dioxide as a source of carbon and purely inorganic materials only. It grows best in a strongly acid medium (pH range about 1.0-6.0) and according to Butlin it can oxidize sulphur until the concentration of the sulphuric acid produced reaches the incredible figure of about 10 per cent (i.e. a negative pH value) and still survive!

**SELF-PURIFICATION OF STREAMS**

When certain kinds of soluble mineral pollution (e.g. sodium chloride) are added continuously to a river, no appreciable change may occur other than the natural dilution which goes on as the river gains in volume in its course to the sea by the ingress of
tributaries and the increase in the total catchment area. Most salts of inorganic acids belong to this category though sometimes chemical changes may take place with other substances in the stream water. For instance, zinc sulphate can react with the natural bicarbonate alkalinity of river water causing some of the zinc to be precipitated from solution. This does not, however, result in the destruction of the mineral matter but merely in its transference from solution to the mud at the bottom of the stream, for under other conditions (e.g. a decrease in pH by an acid discharge) the zinc could pass back from the mud into solution again. On the other hand, when a river receives continuous pollution by organic wastes (e.g. sewage or many organic trade wastes) the course of events is rather different. The river tends to overcome the pollution load, to purify itself, and to recover naturally in the course of time, thus exemplifying the ancient saying that running water purifies itself. Self-purification of rivers, one of the most remarkable of Nature's workings leading to the eventual elimination of the organic pollution, is dependent to a large extent on biochemical reactions brought about by the activities of micro-organisms (especially bacteria) which, given sufficient dissolved oxygen, utilize the organic matter as food and break down complex compounds to simpler and comparatively harmless end-products (cf. page 29). Other factors, such as dilution, sedimentation and sunlight, play a by no means unimportant part in the self-purification of streams. Some rivers are able to undergo self-purification in a fairly short distance, others may require dozens of miles or even more. Self-purification is a complicated process and each river has its own specific capacity for purifying itself which can only be properly evaluated after an extensive chemical, physical, hydrological, and biological survey. The factors influencing self-purification have been discussed by many writers, and will now be considered in some detail.

**DISSOLVED OXYGEN**

Self-purification of a stream is dependent upon the presence of a sufficient quantity of dissolved oxygen. So long as oxygen is not used up too rapidly during the oxidation of organic matter by the activities of bacteria, some improvement in the condition of the stream may be expected. But if the rate of uptake of oxygen is greater than the rate at which oxygen is replenished (e.g. by re-aeration from the atmosphere, by dilution with clean well-oxygenated water, and by photosynthesis) the stream condition will tend to worsen. In extreme cases when all the dissolved oxygen has become exhausted, self-purification will cease and septic conditions
Oil pollution affects self-purification adversely by interfering with re-aeration (see Chapter 3). The experiments of Holroyd and Parker have shown that surface active agents (e.g. synthetic detergents) also have a marked adverse effect on re-aeration. The Water Pollution Research Laboratory have reported that the addition to de-aerated distilled water or sea-water of a mixture of several household washing preparations containing synthetic detergents caused a considerable reduction in the rate of re-aeration when the water was stirred and re-aerated by means of impinging jets of air; as little as 1 p.p.m. of anionic detergent (expressed as sodium lauryl sulphate) reduced the re-aeration coefficient by about 20-30 per cent. There is, therefore, strong evidence that the presence of quite small amounts of synthetic detergents may delay appreciably the rate of recovery of a stream.

The de-oxygenation of river water by the discharge of organic wastes may be a relatively slow process. Hence it happens that the point of maximum de-oxygenation usually occurs a considerable distance (often many miles) below the point of discharge, being determined by such local factors as the dilution, the B.O.D. of the discharge and of the river water, the nature of the organic matter, the total organic load on the river, the physical characteristics of the stream, the extent to which re-aeration from the air occurs, the dissolved oxygen content of the stream, the temperature, and the kind and numbers of micro-organisms present in the discharge (cf. Chapter 8, page 201). Determinations of B.O.D. and dissolved oxygen at various points in the river are necessary to assess the extent to which self-purification has proceeded. The mathematical formulation of the biochemical oxidation going on in polluted streams will be considered later (see pages 147-153).

**Kind of Organic Matter**

The rate of self-purification will depend to some extent not only on the amount of organic matter discharged but also on its character or nature. Oxidation of the more easily decomposed organic matter (e.g. domestic sewage, and wastes containing proteins, sugars and fats) begins as soon as it is discharged to the stream, but some substances are more slowly broken down and a few materials (e.g. lignin and cellulose) are very resistant to oxidation and may take many months to decompose. Finally, a dark brown or almost black complex organic material remains which is generally called "humus"; it forms part of the river mud and is extremely resistant to further decomposition by micro-organisms, taking as long as 10-30
years for complete stabilization. Humus contains carbon, hydrogen, oxygen and nitrogen; the amount of carbon is usually about 58 per cent and the C:N ratio in humus is about 10:1 (i.e. the same as in fertile soil) but much lower in most waste organic materials (usually about 20 or 30:1).

The work of Adeney and others has shown that the oxidation of organic matter during self-purification takes place in two stages. During the first or carbonaceous oxidation stage, about 70-80 per cent of the organic carbon is completely oxidized to carbon dioxide, water and ammonia being also formed from the hydrogen and nitrogen of the organic matter. During the second, or nitrification stage, biochemical oxidation of ammonia to nitrous and finally nitric acids occurs and at the same time the remaining 20-30 per cent of the organic carbon is utilized by the bacteria for their nutrition and growth, and substances of the nature of humus are produced as secondary products.*

BIOLOGICAL FORCES (see also Chapter 8)

Amongst the biological agencies playing a vital role in the self-purification of streams are the following:

**Bacteria**—These are the most important of the micro-organisms which attack the organic matter. It may appear very remarkable that organisms so minute as bacteria should be such efficient scavengers of organic matter in dilute solution. But, as Adeney, quoting Johnstone, has pointed out, the absorption of food by a bacterium most likely takes place over its entire surface and a bacterium has an enormous surface in relation to its weight; calculation shows that 1 kg of dry organic bacterial substance has the tremendous surface area of 62,500 m² whereas in man 1 kg of dry organic substance has a surface area of only 0.168 m².

**Algae**—These belong to the vegetable kingdom and do not break down organic matter. Under the influence of bright sunlight, algae and other green aquatic plants containing chlorophyll play an important part in photosynthesis (page 134) utilizing carbon dioxide and converting it into oxygen, which becomes available for self-purification.

**Protozoa**—These not only ingest dead organic matter but also act as scavengers by feeding on bacteria and algae, thereby helping to maintain a proper biological balance in the stream.

**Rotifers** and **Crustacea** in a similar way prey upon algae and protozoa.

**Worms**—Sludge worms (e.g. *Tubifex*) and bloodworms (*Chironomus*)

* More recent work, however, indicates that oxidation of organic matter and nitrification can proceed simultaneously.
larvae) feed upon sludge deposits at the bottom of the stream and so play their part in breaking down and stabilizing the sludge. Biological aspects of self-purification are discussed in further detail in Chapter 8.

TOXIC SUBSTANCES

Since self-purification is largely dependent upon the activities of bacteria and other micro-organisms, it is evident that the presence of any toxic substances (e.g., acids, alkalis, metallic contaminants, cyanides, phenols, etc.) will tend to reduce the rate of self-purification of a river by killing the organisms or arresting their development. The extent to which the natural self-purification processes are inhibited will depend upon the nature, degree of toxicity, and concentration of the chemical poison. For example, Rogovskaya\(^5\) has shown that more than 1 p.p.m. of TNT in water represses the self-purification of the water but 0.5-1 p.p.m. of TNT retards self-purification only slightly. Again, investigations by Kalabina and others\(^6\) indicate that 0.1-0.5 p.p.m. of copper and 1 p.p.m. of lead are toxic to bacteria and cause appreciable retardation of the processes of self-purification in sewage-polluted river water. The experiments of Grushko\(^7\) have shown that hexavalent chromium may affect adversely biological sewage treatment processes as well as the microflora of river water. Thus the numbers of bacteria in a sewage effluent were reduced by 70 percent in 3 days in the presence of a solution of potassium chromate containing 0.01 p.p.m. of Cr. The effect of chromium was found to be dependent on the type of micro-organism, the form in which the chromium was present, and the concentration of chromium. The inhibiting effect of acid wastes from coal mines on the natural purification of the polluted Schuylkill river, Pennsylvania, U.S.A., was reported by Chubb and Merkel\(^8\). They found that the pH value of this river at Leesport was as low as 4.3 and for some distance de-oxygenation of the water by the breakdown of the sewage and trade wastes present was delayed by the acidity. When, however, the pH value exceeded 7.0, owing to neutralization by alkaline waters from a tributary draining a limestone region, normal bacterial action resulting in de-oxygenation and self-purification took place.

PHYSICAL CHARACTERISTICS OF STREAM

Such physical characteristics as the velocity of the stream current, the depth and cross-section of the stream, the character of the stream bed (i.e., whether gravelly, sandy, etc.) are all important factors which have a marked effect on the rate of re-aeration and therefore on the rate of self-purification. Thus, a shallow fast-flowing
stream will purify itself in a much shorter time than a stream which is deep and sluggish. For example, Wührmann states that a large number of Swiss rivers receiving discharges of sewage effluents are of the shallow turbulent type with gravelly or rocky beds, with a mean water depth often less than 1 ft., and with a velocity of flow greater than 1 ft./sec and usually between 3-6 ft./sec, and these physical conditions result in high re-aeration coefficients (page 152) and rapid self-purification. Krittell and Kohtz carried out studies on the natural purification of a shallow turbulent stream in the Tennessee valley, U.S.A. This stream had an average velocity varying from 0.7-1.36 ft./sec and an average depth of about 2-4 ft. It was found that much more organic pollution could be dealt with by this stream without undue depletion of dissolved oxygen than by a deep sluggish river and this was partly accounted for by the high re-aeration coefficients obtained.

The Water Pollution Research Laboratory is at present carrying out a programme of work on the rates of re-aeration of streams of different types (deep, shallow, and so on).

**Dilution**

The ratio of the volume of polluting liquid to the volume of the stream water is of great significance and when organic wastes are discharged to a stream, dilution plays a fairly obvious though important part in diminishing the objectionable character of the pollution. Dilution may come about through the ingress of underground or surface tributaries and by run-off during wet weather. The diluting water may also prove to be an important means of supplying extra dissolved oxygen, but on the other hand grossly polluted tributaries may turn out to be a liability in this respect.

**Weather Conditions**

Sunlight can play quite an important part in the self-purification of streams. It may act by promoting photosynthesis (page 134) and thus supplying extra dissolved oxygen during the hours of daylight. It might have some adverse effect owing to the possible bactericidal action of ultra-violet light.

Wind action may be of value in promoting wave action on the surface of a river and so increasing the rate of absorption of atmospheric oxygen and producing good mixing.

Some of the greatest difficulties in connection with self-purification occur during drought periods and more particularly when these are associated with high temperatures. Indeed, Velz considers that self-purification studies should include a statistical analysis of droughts for each stream.
Weather conditions will receive more detailed consideration later (see Chapter 11, page 404).

SEDIMENTATION AND SLUDGE DEPOSITS

Sludge deposits on the bed of a stream are formed as a result of sedimentation (i.e. the settlement of suspended matter in sewage and trade wastes) and also by the flocculation of colloidal matter and the formation of insoluble humus as a final decomposition product of organic matter. The oxidation of these deposits can go on for very long periods. Sludge deposits, owing to their high oxygen demand, can affect self-purification adversely by depleting the river water of dissolved oxygen and undergoing anaerobic digestion. Septic action often results in gas evolution causing sludge to rise to the surface. During periods of high river flow after rain, it was found by Mohlman and his associates that the diapсорal of the sludge throughout the river caused a marked fall in the dissolved oxygen content of the river. These authors also made the interesting observation that a rapid fall in barometric pressure caused expansion of gas in the sludge deposits and the sludge rising to the surface increased the B.O.D. of the river water and lowered the dissolved oxygen content.

Velz from theoretical considerations has deduced that

1) at velocities of stream flow of less than 0.6 ft./sec organic sludge deposits are likely to be formed on the stream bed;
2) fresh deposits of organic sludge undergoing digestion can be removed by scouring action at velocities lying between 0.6 and 1.0 ft./sec; and
3) deposits of digested sludge would be removed by scour at a velocity of about 1.3 ft./sec.

Observations made by Velz in connection with the Kalamazoo river gave strong support to these conclusions. It was shown that in a clean stretch of river separating two areas of deposited sludge, the velocity would not fall below the critical 0.6 ft./sec until the run-off had fallen to about 130 ft.3/sec, an occurrence only likely about once in 20 years. Upstream of this clean stretch, however, where sludge deposits do accumulate at times, a velocity below 0.6 ft./sec is reached when the run-off is 700 ft.3/sec or less, which occurs frequently every year. Moreover, run-offs of 700-1,500 ft.3/sec occur frequently enough to cause velocities of 0.6-1.0 ft./sec, i.e. enough to scour fresh organic deposits which are subsequently deposited downstream. There is much accumulation of sludge downstream where channel velocities of 0.6 ft./sec or less only occur when the run-off is less than 1,500 ft.3/sec, which occurs quite often for long periods.
For a discussion of the processes of natural purification of river muds and of the effects of this purification upon the river water, the comprehensive paper by Fair and his co-workers should be consulted.

**Temperature**

Temperature plays a vital part in chemical and biochemical reactions and is an important factor influencing self-purification in streams. According to the well-known van't Hoff rule, the speed of a chemical or biochemical reaction is roughly doubled by a rise in temperature of 10°C. The nitrification of ammonia by microorganisms, the biochemical oxidation of phenol, the germination of seeds, the rate of growth of yeast cells, and the rate of development of fish eggs all follow this rule approximately. As far as biochemical or biological processes are concerned, however, the validity of the rule is often limited to a comparatively small region of temperature in the neighbourhood of 20°C.

Bacteria and other micro-organisms effecting breakdown of organic matter in streams are profoundly influenced by temperature changes and are more active at higher temperatures than at lower temperatures. The rate of oxidation of organic matter is therefore much greater during the summer than during the winter. This means that self-purification will be more rapid, and the stream will recover from the effects of organic pollution in a shorter distance during the warmer months of the year than in the cold days of winter. For a similar reason, as Butcher has pointed out, the growth of 'sewage fungus' takes place over a longer stretch of river during the winter than in the summer. In the winter the organic pollution responsible for the growth of the fungus may be carried many miles downstream before it is completely decomposed whereas at the higher temperatures of the summer breakdown will be complete in a comparatively short distance.

It must be pointed out, however, that since warm water contains considerably less dissolved oxygen than cold water (see page 368) a heavy pollution load is much more likely to de-oxygenate a stream and promote undesirable septic conditions in summer than in winter. Anaerobic decomposition is also profoundly affected by temperature changes. Viehl states that the rate at which putrefaction takes place is four times as great at 27°C as at 8°C, whilst in the region of freezing point very little putrefaction occurs at all. Hence, watercourses containing putrescent organic sludge deposits are particularly liable to suffer from odour nuisance and from unsightly floating masses of decomposing sludge when the temperature of the watercourse rises either in summer or at times when large
volumes of hot effluents are discharged from industrial premises or power stations.

**PHYSICAL CHEMISTRY OF DE-OXYGENATION AND RE-AERATION**

The biochemical oxidation of organic matter in streams, due to the activities of bacteria, can be formulated mathematically if we assume, following Phelps, Theriault and Inkster, that the oxidation is a monomolecular reaction and that the rate at which dissolved oxygen is utilized is directly proportional to the amount of unoxidized carbonaceous matter (measured in terms of oxidizability) present at any time. This oxidation proceeds quite rapidly during the first few days and then slows down until the end of about 20 days (see Chapter 10, Figure 26, curve A). The oxygen demand exerted during the first 20 days is generally called the '1st stage' or 'carbonaceous' B.O.D. Any later demand is due to nitrification, which, however, sometimes takes place earlier and complicates the simple mathematical analysis.

If 

\[ y = \text{the B.O.D. of a sample (p.p.m.) exerted in time } t \text{ days} \]

\[ L = \text{the B.O.D. (p.p.m.) remaining to be exerted at time } t \]

\[ L_0 = \text{1st stage B.O.D.} \]

\[ K_1 = \text{reaction velocity (or de-oxygenation) constant to the base } e \]

\[ k_1 = \text{the constant to the base 10} \]

Then we have

\[ \frac{dL}{dt} = K_1L. \]

Integration of this equation gives

\[ L = L_0e^{-k_1} = L_0 \cdot 10^{-0.1} \]

Hence

\[ y = L_0 - L = L_0 - L_0 \cdot 10^{-0.1} = L_0(1 - 10^{-0.1}) = L_0(1 - 0.023) = L_0(0.977) \]

The reaction velocity constant \( k_1 \) was evaluated by Phelps by statistical analysis of the results of a large number of methylene blue stability tests. The value of \( k_1 \) is usually taken to be 0.1 at 20°C for organic matter of sewage origin, but this is only correct for common logarithms to the base 10 and for time units expressed in days (it would be 0.23 if natural logs to the base e are used). The significance of this figure of 0.1 is that 97.7 per cent or about one-fifth of the oxidizable organic matter present at any time will undergo oxidation during the next 24 hours.

Studies by Streeter and Phelps have shown that in sewage

*For \( y = L_0(1 - 10^{-0.1}) = L_0 \times 0.977.\)
and polluted river waters, the constant $k_1$ varies with temperature in accordance with the equation:

$$k_1(T) = k_1(20) - 1.047T - 20 = 0.1 \times 1.047T - 20$$

where $(k_1)_T = \text{de-oxygenation constant at } T \degree C$

and $k_1 = \text{de-oxygenation constant at } 20 \degree C = 0.1$

This means, for example, a doubling of the rate of oxidation for a temperature rise of $15 \degree C$.

The 1st stage B.O.D., $L_1$, also varies with the temperature, the equation being

$$L_1(T) = L_1(20)(0.02T + 0.60)$$

The use of formulae (1), (2) and (3) enables us to calculate the B.O.D. and rate of de-oxygenation of polluted waters at any temperature and for any period of time. It must be pointed out, however, that several workers have found somewhat different values for the de-oxygenation constant $k_1$. For example, GOTAAS obtained an average value of $0.19$ at $20 \degree C$ in the biochemical oxidation of sewage.* RUCHHOFT, PLACAK and ETTINGER found that nitrification can complicate the biochemical oxidation of sewage as nitrification frequently takes place simultaneously with carbonaceous oxidation during the first 10 days; if an allowance be made for the oxygen involved in nitrite formation, the rate of oxidation of sewage was 'pseudo-monomolecular' but the value of the de-oxygenation constant $k_1$ was shown to vary over a wide range (from $0.07$ to $0.25$ at $20 \degree C$) for different samples of sewage. STREETER states that the de-oxygenation constant can have different values in highly polluted shallow streams and in sludge deposits for which he gives the following values:

<table>
<thead>
<tr>
<th>Highly polluted shallow streams</th>
<th>$k_1$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bottom sludge deposits originating in sewage</td>
<td>$0.01 - 0.05$</td>
</tr>
<tr>
<td>Humoid deposits</td>
<td>$0.001$ or less</td>
</tr>
</tbody>
</table>

GOTAAS in a study of the effect of temperature on the biochemical oxidation of sewage also found that the variation of $k_1$ with temperature for temperatures between $5 \degree$ and $30 \degree C$ could be expressed better by the following equation than by equation (2):

$$k_1(T) = 0.0115T^{0.932}$$

A rather helpful measure of the rate of de-oxygenation, using a

* This means that oxidation of organic matter will be $35.4$ per cent completed at the end of 1 day instead of $20.6$ per cent when $k_1$ is taken to be $0.1$.

† Depends on age of deposits.
term borrowed from radio-chemistry for the rate of disintegration of radioactive elements, is the 'half-life', i.e. the time required for a 50 per cent completion of de-oxygenation, or what amounts to the same thing, the time taken for one-half of the organic matter to be oxidized. The half-life can be easily calculated as follows:

If

\[ t' \text{= the half-life in days} \]

we have, since \( L = I_0 \cdot 10^{-4t'} \) (page 147)

\[ 0.5 = 10^{-4t'} \]

therefore

\[ \log_{10} 0.5 = -k_1 t' \]

therefore

\[ 1 - 699 = -k_1 t' \]

therefore

\[ -0.301 = -k_1 t' \]

or

\[ t' = \frac{0.301}{k_1} \]

Thus, taking \( k_1 \) to be 0.1, the half-life would be slightly over 3 days. The half-life is a convenient measure of the ease or difficulty with which de-oxygenation occurs, or with which the organic pollution in a stream undergoes biochemical oxidation. Obviously, the shorter the half-life, the quicker does oxidation and purification take place.

The form of equation (1) makes it difficult to determine \( k_1 \) and \( L \) from experimental data, i.e. from B.O.D. determinations done on several successive days or at several points along a river. Three methods much used in the past for determining \( k_1 \) and \( L \) are the following:

(i) The Reed-Theriault method of 'least squares'.
(ii) The 'log-difference' method of Fair.
(iii) The 'slope' method of Thomas.

These three methods are laborious and involve very extensive calculations. A fourth method, the 'method of moments' developed by Moore, Thomas and Snow involves relatively simple calculations followed by reference to a number of appropriate graphs which are given in the paper. Perhaps the simplest method of all, a graphical method, has been described by Thomas. He showed that when \( \log \left( \frac{L}{I_0} \right) \) was plotted on ordinary graph paper against \( t \), a straight line was obtained as in Figure 2. The intercept \( A \) and slope \( B \) (Figure 2) are defined by the equation:

\[ A = \frac{1}{2.34k_1 L} \]
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and

\[ B = \frac{(2-3k_t)^{2/3}}{(6L)^{1/3}} \]

from which we get

\[ k_t = \frac{2-61B}{A} \] \hspace{1cm} (4)

and

\[ L = \frac{1}{2+3k_tA^3} \] \hspace{1cm} (5)

Figure 2. Illustrating graphical determination of de-oxygenation constant by method of THOMAS81.

By courtesy of Water and Sewage Works

The procedure given by THOMAS81 for determining \( k_t \) and \( L \) is as follows:

(i) Carry out B.O.D. determinations for 1, 2, 3... days and calculate \( \left( \frac{y}{y_0} \right)^{1/3} \) for each day.

(ii) Plot \( \left( \frac{y}{y_0} \right)^{1/3} \) against \( t \) on ordinary graph paper and draw a straight line through the points.

(iii) Measure \( A \) and \( B \), and substitute the values in equations (4) and (5).

(iv) Finally, calculate \( k_t \) and \( L \) from equations (4) and (5).

Sometimes, owing to lack of proper seeding or other interfering factors, a lag phase appears in the first part of a B.O.D. curve. In such cases, equation (1) becomes

\[ y = L_0 \left[ 1 - 10^{-k_t(t-t_0)} \right] \]

where

\( y \) = residual oxygen,

\( L_0 \) = lag period in days.

Concurrently with de-oxygenation, re-aeration also takes place in a polluted stream and the combined influence of these two factors
causes progressive changes in the dissolved oxygen content of the stream. If the dissolved oxygen content is plotted against the time of flow downstream, a characteristic curve is obtained, termed the 'oxygen sag' curve, typical examples being shown in Figure 3.

Streeter has well described the form of this curve as that of 'an inverted bow with an extended limb reversing its curvature in a downstream direction and approaching an asymptote represented by complete oxygen saturation'. It will be noticed that the curve tends to sag in the inverted bow section and that there is a point at which the dissolved oxygen is at its minimum. The oxygen content at this point will depend upon the extent of the pollution load, and in cases of gross pollution may fall to zero and so the characteristic 'inverted bow' part of the curve may not appear (see Figure 3).

From studies carried out on the Ohio river, Streeter and Phelps developed a mathematical formulation of the oxygen sag curve. On the assumptions that

(a) the rate of de-oxygenation is proportional to the unsatisfied oxygen demand at any time, and
(b) the rate of atmospheric re-aeration is proportional at any time to the dissolved oxygen deficiency at that time,

it follows that the rate of change in the dissolved oxygen saturation deficiency at any time is proportional to the B.O.D. remaining to be exerted and to the dissolved oxygen saturation deficiency. This leads to the differential equation

$$\frac{dD}{dt} = K_1 L - K_2 D$$
where \( D = \) dissolved oxygen deficit in p.p.m. at a point after a time of flow \( t \) days from the beginning.

\[ K_2 = \text{re-aeration reaction velocity constant (base e)} \]

On integration and changing to logarithms to the base 10 we get the expression

\[ D = \frac{k_2 L}{k_2 - k_1} \left( 10^{-k_1 t} - 10^{-k_2 t} \right) + D_0 \cdot 10^{-k_2 t} \quad \ldots \quad (6) \]

where \( k_2 = \text{re-aeration reaction velocity constant (base 10)} \)

\( D_0 = \text{dissolved oxygen deficit (p.p.m.) of the receiving water at zero time} \)

and the other symbols have the meanings previously assigned to them.

Streeter and Phelps\(^7\) in their studies of the Ohio river found that the re-aeration constant, \( k_2 \), was influenced by the velocity of flow, the mean depth, slope and roughness of the channel and the total volume of diluting water. Babbitt\(^3\) states that the value of \( k_2 \) varies from about 0.05 for small backwaters to 0.5 or more for swift streams and rapids. The value of \( k_2 \) is also influenced by variations in stream temperature to some extent and the effect can be calculated by the following empirical formula proposed by Streeter\(^8\) :

\[ (k_2)_{T} = (k_2)_{20} 
\begin{align*}
&\left( \frac{T}{20} \right)^{1.0159} - 20 \\
&= \frac{(k_2)_{T}}{(k_2)_{20}}
\end{align*} \]

where \( (k_2)_{T} = \text{re-aeration constant at } T^\circ C \)

\( (k_2)_{20} = \text{re-aeration constant at } 20^\circ C \)

The calculation of \( k_2 \) can be made by indirect substitution in equation (6); several arbitrary trial values of \( k_2 \) are plotted against calculated values of \( D \) and the required value of \( D \) can be found from the graph\(^8\).

Laboratory studies by Lynch and Sawyer\(^3\) using 50 p.p.m. of various synthetic detergents suggest that these detergents can reduce considerably the re-aeration constant of a stream. This means that re-aeration and therefore self-purification will be slowed down, which might be serious in the case of those detergents which resist biological oxidation (pages 44, 46), as the effect of discharging effluents containing detergents could persist for long distances.

The determination of the point of minimum dissolved oxygen content (i.e. the lowest point on the oxygen sag curve) is obviously of great practical importance in stream pollution problems. By differentiating equation (6) with respect to time and equating to zero\(^8\) we can obtain the time taken to reach this minimum point, \( t_t \):

\[ t_t = -\frac{\log_{10} \left[ \frac{k_2}{k_1} \left( 1 - \frac{D_0 (k_2 - k_1)}{k_1 L} \right) \right]}{k_2 - k_1} \]
Unfortunately lack of familiarity with mathematics and the complexity of the calculations involved have prevented a wider use of the various formulae put forward in the preceding pages. Even Streeter, who has had so much to do with the derivation and application of the formulae, wrote in 1949: 'One of the principal deterrents to the wider use of the oxygen sag equation in connection with stream sanitation problems has been the mathematical complexity of its solution. It has remained to a large extent a classroom problem rather than the practical working tool it should be.'

For details of the practical application of the formulae given in this chapter, the reader is referred to the literature (see references 52, 71, 82, 85, 86, 87, 88). It must, however, be added that these formulae were derived from data obtained in the U.S.A. where rivers are large and sources of pollution are as a rule far apart. In many of the smaller highly industrialized rivers of Britain, it is doubtful whether the practical application of these formulae is justified since the various sources of pollution are likely to introduce too many complications. Moreover, as Price has pointed out, the rapid geographical, climatic and other changes occurring in most of our rivers would tend to cause the re-aeration constant, $k_2$, to vary from mile to mile and even from hour to hour. Also, it is uncertain, as Southgate has emphasized, whether the rate of oxidation of an effluent under natural conditions in a stream is the same as that obtained in laboratory bottle experiments.

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In a long paper which has become a classic on river pollution Ellis\(^1\) cites 114 substances which may be found in stream pollutants. He could have used the expression 'a hundred and one', for the list of substances which may prove dangerous to fish is a very long one and increases with industrial developments. In this chapter the writer discusses the various ways in which stream pollutants may injure or kill fish, the ways in which the biologist attempts to assess their toxicity and the extent to which fish are capable of detecting these substances and avoiding them when escape to normal conditions is possible.

The literature on the subject, though extensive and scattered, is comparatively recent. The long bibliography in Ellis's paper\(^1\) includes very few works published prior to 1910 and the recent reviews by Dooher\(^5\) and Katz\(^5\), in which 281 papers are cited, refer to only 33 published before 1920. It was in 1919 that Carpenter\(^4\) working at Aberystwyth, began a study of the pollution of the rivers of Cardiganshire which seemed to be a result of the lead and zinc mining carried on in the district—an old industry which declined in the latter part of the nineteenth century and had a brief revival during the 1914–18 war. Popular opinion had always associated the absence of fish from certain Cardiganshire rivers with the mining, crushing and washing of lead ores and a theory had been advanced according to which the toxic nature of their waters was due to gritty lead ore carried in suspension, which irritated the gills of fish, setting up inflammation. Carpenter was able to show that the death of fish in the polluted waters was due not to gritty material in suspension but to lead salts in solution. Fish confined in fish cages remained healthy when the water flowing through the cages was free from dissolved lead but died when the lead concentration rose to 0·3–0·4 mg/l. at flood time. It is possible that zinc salts shared the responsibility but methods for detecting
minute amounts of zinc in solution were not available at that time.
Later, Carpenter was able to explain the nature of the toxic action of
heavy metal salts on fish. (It appears that the heavy metal ions
(lead, zinc, copper, mercury, silver, nickel and cadmium) in dilute
solution precipitate the mucous secretions produced by the gills;
the interlamellar spaces become filled with this precipitate and the
normal movement of the gill filaments becomes impossible. The
intimate contact between water and gill tissues which is necessary
for respiration is thus prevented and eventually gaseous exchange
is impeded to such an extent that the fish dies from asphyxiation.)
The course of the toxic process can be studied by placing a fish
in a dilute solution of a heavy metal salt and recording periodically
the rate of the opercular movements. In addition the apparatus
can be arranged to permit regular measurements of the rate at which
the animal is removing oxygen from the solution. Physiologists
have devised some very complicated apparatus for doing this and
these arrangements are necessary if the respiration rate is to be
measured with great accuracy. When we are dealing with the
very great changes in the rate of oxygen utilization which are seen
in these experiments a comparatively simple apparatus as used by
the writer is adequate. Two typical results are set out in Figure 4.
The fish used is the common 3-spined stickleback (Gasterosteus

Figure 4. Oxygen consumption (heavy) and opercular movement rate (light) curves for
sticklebacks in 0.002N copper sulphate and 0.005N lead nitrate. Temp. 17° C. By
courtesy of the Journal of Experimental Biology

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aculeatus), the solutions are 0.002N CuSO₄ and 0.005N Pb(NO₃)₂. These concentrations are much higher than what would be encountered in natural waters but experiments with lower concentrations have a similar result, the time scale being extended.

Normally the stickleback 'breathes' about 120 times a minute at 17° C. The opercular movements are not regular; 5-10 rapid movements will alternate with periods of rest lasting several seconds. When the fish is inactive the rise and fall of the gill covers may be almost imperceptible. When the heavy metal salt is run into the apparatus the rate of opercular movement and the rate of oxygen utilization begins to rise; the increase in oxygen utilization is probably due to increased activity, for the fish seems to sense the unfavourable change in its environment and will struggle. As the toxic process takes effect the respiratory movements become more and more rapid, more regular and of increased amplitude. Despite

Figure 5. Oxygen consumption and opercular movement rate curves for a stickleback immersed in 0.0001N mercuric chloride for 50 minutes, after which the solution is replaced by water and the fish recovers. Temp. 17° C. By courtesy of the Journal of Experimental Biology

the animal's efforts to maintain its oxygen supply the oxygen consumption now fails, returns to normal and becomes sub-normal. After periods of struggling and rest and minor ups and downs in the opercular movement rate the fish sooner or later becomes exhausted; when the oxygen consumption sinks to about 20 per cent normal the opercular movement rate begins a precipitous descent and the fish dies. If the subject of experiment is removed from the solution before the toxic process is too far advanced and placed in well aerated water, or if water is run through the apparatus to replace the solution, a slow recovery may take place. Figure 5 records the recovery of a fish after a 50-minute exposure to a mercuric chloride solution and shows how the restoration of the
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efficiency of the gills leads to a slow recovery in the oxygen utilization rate and a slow decline in the rate of opercular movement. The extent to which this gill-clogging film of mucus is developed depends on the species of fish under experiment and its general level of metabolic rate. Fishes of high metabolic rate, exacting in their oxygen demands, will not show any great accumulation of material on the gills after death in these solutions. Fishes of very low metabolic rate, tolerant of oxygen deficiency, like the goldfish, will show much more definite symptoms. Goldfish placed in dilute lead nitrate solutions (10 mg/l) will develop a white, woolly deposit on the gills; precipitated mucus will coat the body and quantities of this will be shed off making the solution faintly milky. (Heavy metal salts in solution constitute a very serious form of pollution for they are stable compounds, not readily removed, and in soft waters are fatal to fish at very low concentrations. Copper salts are toxic to sticklebacks down to 0.02 mg/l. Mercury and silver salts are even more toxic, lead and zinc salts less so. Metallic pollution may persist for years after mining operations have ceased. In the case of the River Ystwyth, in north Cardiganshire, streamlets flowing through old mine workings and drainage from ‘dumps’ of crushed ore continue to maintain the river in a polluted condition over 25 years after the closing down of the last mine worked in the Ystwyth valley. At the time of writing (1953) the river water at low level contains no detectable amount of lead but still carries up to 1 mg/l. (1 p.p.m.) of zinc in solution.

Recent work in Australia by Affleck has shown that zinc compounds are highly toxic to the ova and alevins of rainbow trout. It is stated that as little as 0.01–0.02 mg/l. may be fatal. Affleck’s observations confirm earlier work by the writer showing that the toxicity of lead and zinc salts is greatly reduced in the presence of soluble calcium compounds. Sticklebacks die in about 24 hours in a 1 mg Pb per litre solution of lead nitrate in soft water, but if 50 mg/l. of calcium is present, as chloride, nitrate or bicarbonate, they will live for about 10 days—the survival time of controls. Calcium has a similar effect on the toxicity of zinc, but whether it will reduce the toxicity of copper and other heavy metals has not been tested. Nevertheless it is clear that the hardness of the water concerned is a very important factor when we are dealing with metallic pollution. How soluble calcium compounds exert this protective effect is not completely understood, but it would appear that they interfere in some way with the coagulation of the gill secretions by the heavy metal1.

* Note, however, that the waters used were rather acid and had a low content of mineral salts. Other workers report much higher values (see page 32, also Table 35).
As a second category we may consider the toxic effects of organic and inorganic acids. Ellis\(^1\) has made an extensive series of experiments with goldfish, using eleven different acids found in industrial wastes; his work and that of many others is reviewed by Doudoroff and Katz\(^2\). In the case of strong mineral acids in which the anion is comparatively innocuous (HCl, H\(_2\)SO\(_4\), HNO\(_3\)) the essential factor is the hydrogen ion concentration. Goldfish will survive in solutions of sulphuric acid of about pH 4-0 and hydrochloric acid of about pH 4-5. Sticklebacks can probably survive indefinitely in hydrochloric acid solutions of pH 5-2-5-4. Doudoroff and Katz conclude that 5-0 is approximately the critical pH value for most species of freshwater fishes. Higher hydrogen ion concentrations (i.e., lower pH values) apparently produce a coagulation of gill secretions and asphyxiation, or may exert an astringent or corrosive effect upon the gill tissues with a similar result. Exposure to concentrated solutions of mineral acids will result in such damage to the gills that recovery is not possible. Ellis\(^1\) has shown that the toxicity of many acids is due to their anions or undissociated molecules and in such cases the hydrogen ions may be comparatively unimportant. Thus oxalic acid is lethal because it precipitates calcium salts, removing from solution in protoplasm an element essential for life; tannic acid and chromic acids are examples of acids in which the anions or undissociated molecules form insoluble compounds with certain protein constituents of the living cells of the gill tissues. Acetic acid owes its high toxicity to its high penetrating powers, entering living cells so rapidly as to produce much swelling and it would seem that in this way it can provoke an acute congestion of a fish's respiratory organs. Ellis's discussion of his results is confused by one error; he refers to the \textit{anions} of these acids when it is evident from his argument that he really means \textit{anions}.

Salts which by hydrolysis bring about a marked increase in the hydrogen ion concentration may be lethal simply as a result of this. In a series of experiments with ferric chloride the writer\(^6\) found that the toxicity of solutions of this compound to sticklebacks was approximately equal to that of hydrochloric acid solutions of the same pH.

All the substances so far considered kill fish by impairing the animal's ability to obtain oxygen from the surrounding water. Now we may consider a very important pollutant which kills fish in an essentially different way. Hydrogen cyanides and soluble cyanides enter the body through the gills and the lining of the mouth, circulate in the blood stream and, by some specific inhibitory effect upon certain enzymatic oxidative processes, render the tissues more or less incapable of utilizing the oxygen brought to them. In
addition to this general effect on tissue respiration, experiments on
the frog, which is very resistant to asphyxiation, tend to show that
cyanides also exercise a paralysing effect on the central nervous
system. The effect of sodium cyanide solutions upon the respiration of
Gasterosteus is shown in Figure 6. It will be noted that even a
0·00004N solution brings about a considerable depression of the
oxygen consumption, which sinks to about 32 per cent of normal in
about 90 minutes. This is about the critical concentration at 17°C.
At lower concentrations the fish may survive a very long time in a
condition resembling anaesthesia; they lie almost motionless on
their sides breathing very slowly and feebly. Higher concentrations
are quickly fatal for the respiratory movements may stop abruptly.

Figure 6. The effect of five different concentrations of sodium cyanide on the oxygen con-
sumption of the stickleback. In each experiment ten small fish were placed in the respiration
chamber. The pH of each solution was adjusted to 7·0 by adding sufficient hydrochloric acid.
Temp. 17°C. By courtesy of the Journal of Experimental Biology

Figure 7 is a record of the effect of 0·00005N NaCN upon the oxygen
consumption and opercular movement rate of a stickleback and
presents an interesting contrast to the clinical picture of Figure 5.
There is a preliminary rise in the frequency of the breathing move-
ments but after a few minutes this falls sharply and 30 minutes
from the start of the experiment the rate sinks to 40 per minute.
The oxygen consumption is reduced to 40 per cent normal. On
passing water through the apparatus a recovery begins and about
50 minutes later things are back to normal. The recovery power
of fish after exposure to dilute cyanide solutions is remarkable.
Fish whose breathing movements have become very slow and feeble
and which lie on their sides in a moribund condition will soon
begin to pant energetically on transference to well-aerated water.
In about 20 minutes they regain their sense of balance and start
swimming around and in an hour or two they seem quite normal.
It would seem that the poison can be eliminated from the body very quickly; this may have something to do with the fact that freshwater fish are continually excreting copious amounts of urine. HERBERT and MERKENS, who have used an elaborate constant-flow apparatus for studying the effect of cyanide solutions on rainbow trout, have also noted that the fish would regain their equilibrium in a few minutes if they were removed from the solutions before breathing ceased. An earlier study of the effects of cyanide solutions on rainbow trout is that of ALEXANDER, SOUTHGATE and BASINDALE. An important post-mortem symptom of fish killed by cyanide is the unusually bright red colour of the gills. This is a result of the changes in the condition of the arterial blood brought about by the inhibition of oxidation in the body tissues. For a detailed account of the post-mortem symptoms of fish dying from cyanide poisoning this paper may be consulted and also the paper by BASINDALE, SOUTHGATE and PENTELON.

It has been claimed that in solutions of hydrogen cyanide and soluble cyanides the toxicity may be ascribed chiefly to the action of undisassociated molecules of HCN, which are said to have a much greater power of penetrating living tissues than dissociated ions. Sodium cyanide, potassium cyanide and other soluble cyanides form hydrogen cyanide on solution in water; the extent of this hydrolysis (KCN + H₂O = K⁺ + OH⁻ + HCN) is greatly influenced
by the pH of the solution, being increased with an increase in acidity, depressed by the addition of alkalies. It should follow that the toxicity of cyanides should vary with the pH of the solution. Wurmann and Woker found this to be so in their experiments with Squalin cephalus (the chub) in solutions containing 0.66 mg/l. of CN the toxicity was almost doubled on changing the pH from 8.84 to 7.58. Southgate, however, found that potassium cyanide solutions had approximately the same toxicity to trout over the pH range 6.0-8.5.

Hydrogen sulphide and soluble sulphides have a similar effect to cyanides in that they inhibit oxygen utilization. Here again there is evidence that the undissociated molecule of H₂S appears to penetrate living tissue more rapidly than sulphide ions. Thus in experiments to test the penetration of hydrogen sulphide into cells of the alga Valonia it can be shown that the rate of entrance of total sulphide into the sap is proportional to the concentration of molecular H₂S in the external solution. Longwell and Pentelow studied the effect of sulphides on brown trout and found that the toxicity of a sodium sulphide solution containing 3.2 p.p.m. of sulphur was greatly increased on changing the pH from 9.0 to 6.0. At pH 9.0 the overturning time of the fish was about 120 minutes, at pH 7.0 this time is reduced to about 8 minutes and at pH 6.0 to about 4 minutes. For further information on the way the toxicity of sulphides is influenced by the nature of the water and other substances present the review by Doudoroff and Katz should be consulted. The writer's experiments with sticklebacks show that the critical concentration for solutions of pH 7.0 is about 0.0002N (Na₂S), when the oxygen consumption falls to about 33 per cent normal in 90 minutes. More dilute solutions are tolerated for rapidly increasing times; concentrated solutions are quickly fatal, thus a stickleback placed in a 0.001N solution ceases breathing in 6 minutes. As in cyanide solutions the opercular movement rate falls with the oxygen consumption and fish exhibit a remarkable power of recovery provided they are removed from the solution before they cease breathing.

Aspects of River Pollution

Wells states that carbon monoxide may be present in effluents from gasworks and that it is highly toxic to fish. The extreme toxicity of this gas to man is well known; it is said to have an affinity for haemoglobin which is some 250 times that of oxygen and thus it can reduce enormously the oxygen-carrying power of the blood. The physiological effect of carbon dioxide on fish has been much studied but is not well understood and the experimental results and conclusions of different investigators are not in agreement. In high concentrations (air mixture containing 10 per cent CO₂) the gas is quickly fatal to man, causing a sudden cessation of
respiration and paralysis of all the body functions, but whether
carbon dioxide has some such specific effect on fish has not been
demonstrated. King found that concentrations up to 200 p.p.m.
had no apparent effect on trout. There is, however, evidence that
in the presence of an abnormally high concentration of carbon
dioxide the ability of fish to extract oxygen from the water, when the
oxygen supply is limited, is appreciably impaired. Very different
results were obtained with different fish. From a consideration of pollutants which interfere with respira-
tion when oxygen is available in the water we may go on to consider
those which do not interfere with the mechanism of respiration but
reduce the oxygen supply. Sewage, milk washings and other
organic wastes can reduce the oxygen content of stream water to
a marked degree, even to zero. Thus Werge found that many
samples of water from the Mississippi, just below Minneapolis,
contained no oxygen. The essential biological factor here is the
tolerance of different fish to oxygen deficiency. Loaches are said
to be able to live in water containing little or no oxygen for they
swallow a series of air bubbles at the surface and these bubbles
passing through the gut aerate the blood circulating in the blood
vessels of the intestine wall. Eels are very tolerant of oxygen
deficiency and it is well known that the goldfish depends for its
existence on its ability to survive in very poorly aerated water.
Other coarse fish such as tench, roach and pike are less tolerant
and the species most exacting in their requirements are probably
the salmonids. Ellis made 5,809 oxygen determinations at 982
stations on rivers and streams of the United States and found that
in the warm season of the year, the waters at 96 per cent of the
stations where a good, mixed fish fauna was seen, carried at least
3 mg/l. of dissolved oxygen.

In considering the oxygen requirements of fish the temperature
factor is of great importance. Fish are poikilothermic and their
metabolic rate increases rapidly with rising temperatures. A rise
of 10°C results in the oxygen intake of rainbow trout increasing
to 2.7 times its former value. At the same time a rise of tempera-
ture reduces the amount of oxygen that water can hold in solution,
which makes matters worse. At 4°C water saturated with air
contains about 12.2 mg O₂ per litre, at 10°C about 10.9 mg/l. and
at 24°C 8.3 mg/l. The effects of pollution by organic matter there-
fore tend to be much more serious at high temperatures. Fish
generally react to a deficient oxygen supply by breathing more
rapidly, more regularly and more energetically; in some cases only
the rate of movement changes, in some cases only its amplitude.
Minnows in deoxygenated water will breathe nearly 300 times per
minute. A further response frequently noted is an increased
tendency to swim; this is because movement forward assists the flow of water through the mouth and gill chambers. It is said that the mackerel performs no opercular breathing movements and maintains the circulation of water over the gills by swimming along with its mouth open. The higher the temperature the more swiftly does dyspnoea develop if the oxygen supply fails. At 3°C trout fry take several minutes to react to water containing only 1.8 mg/l (14 per cent saturation); at 20°C they react immediately with staggering movements and violent gulping. It is a simple matter to find out how long fish can live in completely deoxygenated water, for all the investigator has to do is to shut them up in bottles of water from which all the air has been removed with a vacuum pump or by boiling, but few experiments have been carried out to ascertain how long fish can live in water when the oxygen tension is maintained at a constant, abnormally low value, for it is not easy to devise an apparatus which will supply a constant flow of water from which a predetermined amount of the air has been removed. Such an arrangement was devised by SHELFORD and a fractionating column for such experiments has been described by Fry. Alexander, Southgate and Bassindale found that rainbow trout could survive over 30 days in water 37.5-58 per cent saturated at 14.5-17°C and at 4.5°C the fish were apparently unharmed by 68 hours immersion in water only 25 per cent saturated. Within certain limits a reduction of the oxygen tension does not affect the respiration rate in the trout; provided it does not fall below 70 per cent saturation the animal seems able to remove from the water the normal amount of oxygen required. Many workers have investigated the toxicity of ammonia and ammonium compounds to fish with varying results. Here again the problem is complicated by the dissociation and hydrolysis of the salts and it has been shown that the toxicity seems to depend on the concentration of non-ionic ammonia or ammonium base. It would seem that ammonia acts on fish as a true internal poison, entering the body via the gills and circulating in the blood stream, for its toxicity seems to be strictly correlated with the permeability of the gills for the toxic molecules. In man, ammonia is said to destroy the blood corpuscles, haemoglobin is changed into haematin and the blood becomes incoagulable. The inhalation of considerable quantities of the gas can provoke a spasm of the glottis and such swelling and congestion of the mucous membranes of the larynx and trachea that death may occur very suddenly from asphyxia. It is possible that fish are affected in a similar way. Sticklebacks in ammonia solutions die suddenly with widely opened mouths and it has been noted that perch die with the gill covers raised revealing the highly congested condition of the gills.
There remains a long catalogue of substances which occur in polluting effluents and whose effect on fish is not completely understood. Sodium hydroxide and other strong alkalis probably produce asphyxiation by coagulation of gill secretions. Aluminium salts have a similar action, partly due to aluminium ions and to hydrogen ions formed by hydrolysis; aluminium salts are well known astringents. Aniline, which may occur in effluents from gas works and dye works, is very toxic to fish which are at first stimulated and then intoxicated, lying on their sides with their fins and gill covers moving feebly. In man it is said to have a direct effect on heart muscle, producing arrhythmia and heart-block.

Arsenic, which may be present in stream-water as a result of contamination with sheep-dip, arsenical insecticides and weed killers, is said to act as a cumulative poison reaching the gastrointestinal tract in water that is swallowed. Barium salts bring about a spasmodic contraction of involuntary muscles, in addition they bring about a constriction of the arterioles and thus the circulation of the blood is obstructed and the blood pressure raised; this, in fatal cases, seems to be the cause of internal haemorrhages.

Chlorine is a well-known irritant poison producing severe pulmonary congestion and oedema in man. Concentrations of free chlorine as low as 0.5 p.p.m. are said to be very toxic to trout. Ethyl alcohol, which may be present in fermenting organic wastes, rapidly produces intoxication in fish; sticklebacks placed in a 4 per cent solution fall over on their sides almost immediately and their breathing movements become slow and irregular. From this unhappy state they can recover in a few minutes if replaced in water.

Oxalates, as stated previously, disturb calcium metabolism. Phenol and the cresols, which may be present in effluents producing disinfectants, are very toxic. As phenolic substances are so extensively employed as antiseptics there has been much study of their effects on different organisms and tissues. Phenol has an irritant action on mucous membranes and in sufficient quantities may provoke irritation and sloughing; in addition it appears to have some direct effect on the nervous system of higher animals. In frogs convulsions are produced as a result of increased irritability of the spinal cord, leading later to complete paralysis. In mammals muscular tremors are produced at first, later there are convulsions and the respiratory movements become slow, irregular and weak. Death results from asphyxia. In man, small doses may bring on depression, nausea, vomiting, giddiness and irregular respiration leading to collapse and respiratory failure. Most investigators are agreed that these substances seem to have some specific effect on the nervous system of fish. Sticklebacks placed in a dilute solution of phenol almost immediately lose their sense of balance.
and fall over on their sides; they may live for some time in a helpless condition, breathing feebly and irregularly, recoiling violently if touched. Even a brief exposure to very dilute phenol or cresol solutions may result in wild, unco-ordinated swimming; the fish, with bodies twitching spasmodically, will dash in any direction.

In summing up this review of fish toxicology it may be noted that there is a fair amount of evidence suggesting that substances that are not ionized enter their bodies most readily. Freshwater fish normally swallow little or no water but have a dilute and copious urine. The osmotic pressure of their body fluids is much higher than that of the surrounding medium so that considerable quantities of water pass in, mainly through the gills, for the scale-covered integument is relatively impermeable. In this way the entrance of toxic substances may be facilitated and as the blood circulation of a fish is so arranged that blood leaving the gills is immediately delivered by the dorsal aorta to all parts of the body it is not surprising that they can produce their effects so rapidly.

In experimental work to test the toxicity of solutions to fish four criteria have been employed. (1) The immersion time apparently necessary to initiate the toxic process may be measured, that is the time that passes before the first clear indications of poisoning are evident. In the case of heavy metal solutions this would be the time at which respiratory distress begins. (2) The time taken for the toxic process to advance to some well-marked level. Thus in the case of cyanide solutions the experiment might aid in determining the immersion time necessary to depress the oxygen intake to some critical fraction of the normal value. In research on the toxicity to trout of a great variety of substances, the time at which the fish lose their sense of balance and float upside-down (the overturning time) is a much used criterion. This has the advantage that most of the fish recover on restoration to water and can be returned to the river or used again, but in the latter case great care must be taken to avoid acclimatization. The writer has been told the improbable story of wise trout which turned upside-down immediately on being placed in anything but the stock aquarium! The overturning time is not an ideal criterion for general use as the nature of the toxic action of the poison concerned influences the result considerably. In the case of substances which do not affect the nervous system, such as heavy metal salts, the fish do not lose their sense of balance until the toxic process is very far advanced; in phenolic substances the overturning time may be a very small fraction of the survival time. Thus minnows will lose their sense of balance in about 8 minutes in a 0.004 per cent solution of ortho- cresol but are still alive in 5 hours. (3) A series of experiments can be made to determine the minimum time of exposure necessary...
to carry the toxic process so far that recovery is no longer possible. Such times have been called the 'lethal times' or 'fatal immersion periods'. Experiments on these lines may be useful when we are concerned with intermittent pollution, but necessitate more experimental work and more animals. (4) Lastly we may determine the 'survival time', the time of immersion necessary to kill the fish; death is usually assumed when the animal ceases breathing or no longer moves after mechanical stimulation. The value of this criterion again depends on the poison employed. In some cases the death point is well defined, in others it may be extremely vague as the fish may persist for long periods in something like deep anaesthesia.

Fish exhibit a considerable degree of individual variation in resistance to toxic substances. Even if specimens of the same sex and size are selected for experiment there may be considerable differences in individual survival times. WUHRMANN and Woker 33 have made a special study of this aspect of the problem; in their study of the toxicity of ammonia they used about 100 fish for each experiment and concluded that the minimum number of test fish that may be used in any one experiment should not be less than 5 but preferably 10. With certain poisons having less definite effect they consider a still greater number is required. Variation in resistance with the period of acclimatization to the experimental temperature may also have to be taken into account.

If the scientist is to be able to forecast the possible effects of pollution on fishes it is obvious that experiments to test the toxicity of the substance concerned at any single concentration cannot be adequate; it is necessary to have data showing how the toxicity varies with the dilution. POWERS 34, after a long series of trials with goldfish, using a considerable variety of salts, acids and drugs, concluded that over a certain range of values the survival time is inversely related to the concentration. If a graph is drawn in which concentrations are plotted as abscissae and reciprocals of survival times as ordinates the points approximate to a straight line (Figure 8) which cuts the concentration axis at a point which may be called the 'theoretical threshold of toxicity'. The relation between survival time and concentration can be represented by the equation \((c - a)t = K\) where \(c\) is the concentration, \(a\) the theoretical threshold, \(t\) the survival time and \(K\) is a constant. At low concentrations, however, the observed survival times are shorter than this equation demands and at high concentrations the observed times are longer than the theoretical values. Consequently the graph obtained by interpolating the experimental results is more or less sigmoid, only its middle portion being straight. At some concentration value, below the theoretical threshold, the survival time...
becomes indefinite and its reciprocal is zero; this is the true 'threshold concentration'.

Experimental results do not always interpolate to a curve of this type. An examination of Powers's figures for a number of the substances tested raises doubts about the high concentration bend of the sigmoid and there are instances (particularly those for caffeine, phenol, pyridine, sodium nitrate and magnesium chloride) where the interpolation of the experimental results as sigmoid curves is hardly justified. Other workers have obtained varying results on plotting concentration values against the reciprocals of the survival times, overturning times, etc. Herbert and Merkens in their work on the toxicity of cyanides to rainbow trout have drawn a sigmoid curve which they consider to be similar to the results obtained by Powers. Alexander, Southgate and Bassindale also give a graph showing the relation between overturning time and concentration based on their experiments with rainbow trout in potassium cyanide solutions; this graph has no linear portion. GRINDLEY found that the concentration–overturning time relation for minnows placed in solutions of sodium arsenite, sodium dinitrophenate or sodium picrate was linear over a considerable concentration range. A similar result was obtained with rainbow trout using potassium chromate, but not with potassium dichromate. Carpenter found that when the reciprocals of the survival times of fish killed in solutions of heavy metal salts are plotted against the concentrations a curve is obtained which is essentially different from Powers's curves. The survival time (t)–concentration (c) relationship in this case seems to answer to the equation \( \frac{1}{t} \log \left( \frac{1}{c} \right) = K \), where \( K \) is a constant. WURMANN and WOKER also found that the toxicity–concentration relationship is logarithmic in their work on the toxicity of phenol to fishes.

It would seem that Powers's generalization is far too sweeping.
As different toxic substances may have essentially different effects we can hardly expect their toxicity-concentration relationships to be mathematically similar, and when the effect of any substance on fish is studied, experiments should be carried out over an adequate concentration range. Estimates of the toxicity of untested concentrations by the extrapolation of curves are very unreliable. One cannot assume with safety that the survival time will always increase at greater dilutions let alone how fast it will do so. The writer has shown that over the concentration range 0.04–0.0015N the toxicity of copper nitrate solutions to toad tadpoles increases with dilution, at lower concentrations the survival time lengthens so that at 0.0003N it is equal to that at 0.04N. Usually, of course, the survival time does increase more or less progressively at greater dilutions and eventually a concentration is reached where the toxic substance has no definite toxic effect. The fish do not exhibit any symptoms and if the experiment is prolonged they live as long as controls. This concentration is the true threshold. (Figure 9.)

Figure 9. A series of survival curves for the stickleback in salts of the heavy metals. The curves are plotted to dilutions at which the survival times of the fish are approximately equal to that of controls in tap-water—about ten days. The thresholds indicated by the dotted vertical lines are mg/l., or p.p.m., of silver, mercury, cadmium, etc., not mg/1. of salt. The solutions of chloramine A and (gold chloride) were sufficiently acid to be fatal at high concentrations; the relevant portion of this survival curve is indicated by shading. pH of all other solutions within the range 6.0–6.8. Temp. 15–18°C. By courtesy of the Journal of Experimental Biology.
It is very probable that the threshold concentration for any substance and any species of fish varies somewhat with the age of the animals, their physiological condition, the chemical nature of the water used for making up the solution, the temperature and other factors. Consequently any data given for 'threshold concentrations', 'lethal limits', etc., must be applied with caution. The exact limits of toxicity, even at one specified temperature, have been determined for few substances and fishes, but many investigators have carried out experiments down to concentrations at which the survival time or overturning time is a number of hours and is lengthening rapidly on dilution so that some very approximate figures for a fair number of important polluting substances can be tabulated. (Table 35.) The chief test animals cited are brown trout, rainbow trout, minnows, sticklebacks and goldfish. Of these five it is probable that the first four are more or less of the same order of sensitivity; this statement is made cautiously and should be accepted as something requiring confirmation by experimental work. The goldfish is probably rather more resistant; this may be remembered in referring to the table for if any concentration quoted is definitely toxic to goldfish it is very probable that it is even more lethal to the trout.

Man is very sensitive to the presence of some of the irritant toxic gases such as ammonia, sulphur dioxide and chlorine. Other poisonous gases such as carbon monoxide and hydrogen cyanide are not recognized and are consequently much more dangerous. Some years ago it was realized that fish might be able to detect and avoid harmful substances in the surrounding water and experiments were begun to discover whether this is so. The question is of some interest in relation to river pollution particularly when the pollution is temporary or localized. Zones of clean water can be formed at the mouths of tributaries and the tributaries themselves may form a safe refuge to which some fish, at least, can escape if they recognize and avoid the danger. The mainstream of a polluted river is a much greater danger to the fish living in its tributaries if they venture into it. The first apparatus used in these experiments was the 'gradient tank'. This was a long, rectangular tank measuring about 120 cm by 15 cm by 13 cm deep. The front of the tank was made of plate glass to permit observation of the fish. Water flowed in at one end and a solution of the substance being tested flowed in at the other end. An outflow was provided in the middle, water and solution mixed together in the greater part of the tank so that a concentration gradient was established ranging from untreated water at one end to the maximum concentration of the toxic substance at the other. In each experiment a single fish was placed in the apparatus and its behaviour was watched. To record its
### Table 35. Lethal limits to fish for some important polluting substances

In this table the concentration values are the lowest at which definite toxic action is indicated by the data in the reference cited. Except in cases where the 'less than' sign is inserted the survival times or overturning times are at least 6 hours. It should not be assumed that lower concentrations are harmless; the table is designed to give an approximate indication of the degree of toxicity of the substances included and, wherever possible, the works cited should be consulted for further information. Where no reference is given the figures are based on unpublished work by the writer.

Except where otherwise indicated concentrations are parts per million (mg. per litre). (See also Figures 16 and 17.)

The goldfish used by Ellis is the common goldfish, Carassius auratus, but Powers used the common carp, Carassius auratus L. The stickleback is the common 3-spined stickleback, Gasterosteus aculeatus L. The minnow is Phoxinus phoxinus L. The perch is Perca flavescens L. The brown trout is Salmo trutta L, and the rainbow trout is Salmo irideus Gibbons.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Fish tested</th>
<th>Lethal concentration</th>
<th>Temp. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>goldfish</td>
<td>423</td>
<td>18-25</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>stickleback</td>
<td>100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Aluminium nitrate</td>
<td>goldfish</td>
<td>0.1 Al</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Ammonium hydroxide*</td>
<td>goldfish</td>
<td>2-2.5 NH₃</td>
<td>?</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>perch</td>
<td>&lt; 15 (NH₄⁺)</td>
<td>?</td>
<td>29</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>various spp.</td>
<td>2-25 NH₃</td>
<td>?</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>rainbow trout</td>
<td>500 NH₃</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>goldfish</td>
<td>1,000 NH₃</td>
<td>18</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>minnow</td>
<td>200</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td></td>
<td>brown trout</td>
<td>100</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Arsenic compounds:</td>
<td>minnow</td>
<td>17-8 As</td>
<td>12-3</td>
<td>35</td>
</tr>
<tr>
<td>Sodium arsenite</td>
<td></td>
<td>254 As</td>
<td>16-20</td>
<td>35</td>
</tr>
<tr>
<td>Sodium azide</td>
<td>goldfish</td>
<td>10,000</td>
<td>20-3</td>
<td>34</td>
</tr>
<tr>
<td>Barium chloride</td>
<td>stickleback</td>
<td>500 Ba</td>
<td>15-16</td>
<td>9</td>
</tr>
<tr>
<td>Barium nitrate</td>
<td>goldfish</td>
<td>20</td>
<td>18-21</td>
<td>1</td>
</tr>
<tr>
<td>Butyl alcohol</td>
<td>stickleback</td>
<td>0-3 cc/l.</td>
<td>21-5</td>
<td>34</td>
</tr>
<tr>
<td>Cadmium nitrate</td>
<td>stickleback</td>
<td>0-3 Cd</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Calcium nitrate</td>
<td>goldfish</td>
<td>1,000 Ca</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Calcium chloride</td>
<td>goldfish</td>
<td>7,732</td>
<td>21</td>
<td>34</td>
</tr>
<tr>
<td>Calcium hydroxide</td>
<td>various spp.</td>
<td>&lt; 100 (pH 11-1)</td>
<td>?</td>
<td>46</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>brown trout</td>
<td>0-66</td>
<td>?</td>
<td>43</td>
</tr>
<tr>
<td>Chlorine (fry)</td>
<td>rainbow trout</td>
<td>&lt; 0-03</td>
<td>?</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>goldfish</td>
<td>2</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>894</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>stickleback</td>
<td>0-02 Co</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 0-03 Ca</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>goldfish</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0-25 cc/l.</td>
<td>21-5</td>
<td>34</td>
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### Table 35—cont.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Fish tested</th>
<th>Lethal concentration</th>
<th>Temp. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric chloride</td>
<td>stickleback</td>
<td>pH 4.8</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>goldfish</td>
<td>pH 4.0</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Hydrogen sulphide (see also Figure 17)</td>
<td></td>
<td>&lt; 100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Lactic acid</td>
<td></td>
<td>654</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Lead nitrate</td>
<td>stickleback</td>
<td>0.33 Pb</td>
<td>?</td>
<td>5</td>
</tr>
<tr>
<td>Magnesium nitrate</td>
<td>goldfish</td>
<td>0.1 Pb</td>
<td>?</td>
<td>8</td>
</tr>
<tr>
<td>Nickel chloride</td>
<td>goldfish</td>
<td>0.033 Pb</td>
<td>?</td>
<td>1</td>
</tr>
<tr>
<td>Nickel nitrate</td>
<td>stickleback</td>
<td>1 Ni</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>minnow</td>
<td>pH 5.0</td>
<td>?</td>
<td>5</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>perch</td>
<td>&lt; 20</td>
<td>?</td>
<td>29</td>
</tr>
<tr>
<td>Oxygen</td>
<td>rainbow trout</td>
<td>&lt; 0.001</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Phenolic substances:</td>
<td></td>
<td>eel</td>
<td>17-25</td>
<td></td>
</tr>
<tr>
<td>Ortho-cresol</td>
<td>minnow</td>
<td>0.003</td>
<td>?</td>
<td>45</td>
</tr>
<tr>
<td>para-cresol</td>
<td>perch</td>
<td>0.01</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>rainbow trout</td>
<td>60</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>minnow</td>
<td>20</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Phenol</td>
<td>perch</td>
<td>5</td>
<td>?</td>
<td>12</td>
</tr>
<tr>
<td>Phenol</td>
<td>perch</td>
<td>20</td>
<td>17</td>
<td></td>
</tr>
<tr>
<td>Potassium chromate</td>
<td>perch</td>
<td>&lt; 9</td>
<td>?</td>
<td>12</td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>goldfish</td>
<td>100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Potassium nitrate</td>
<td>rainbow trout</td>
<td>75</td>
<td>18-35</td>
<td></td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>goldfish</td>
<td>57</td>
<td>18-35</td>
<td></td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>perch</td>
<td>20</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>perch</td>
<td>6</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Pyridine</td>
<td>perch</td>
<td>&lt; 0.001</td>
<td>?</td>
<td>1</td>
</tr>
<tr>
<td>Quinoline</td>
<td>perch</td>
<td>&lt; 0.001</td>
<td>?</td>
<td>1</td>
</tr>
<tr>
<td>Silver nitrate</td>
<td>perch</td>
<td>&lt; 0.001</td>
<td>?</td>
<td>11</td>
</tr>
<tr>
<td>Sodium chloride</td>
<td>goldfish</td>
<td>75 K</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Sodium cyanide</td>
<td>perch</td>
<td>&lt; 20</td>
<td>?</td>
<td>12</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>perch</td>
<td>10</td>
<td>?</td>
<td>29</td>
</tr>
<tr>
<td>Sodium fluoride† (see also Figure 17)</td>
<td></td>
<td>&lt; 0.001</td>
<td>17-25</td>
<td>1</td>
</tr>
<tr>
<td>Sodium hydroxide† (see also Figure 17)</td>
<td></td>
<td>pH 10-9</td>
<td>?</td>
<td>46</td>
</tr>
</tbody>
</table>

* * These are said to be the minimum tensions at which the animal is able to extract its normal requirement of oxygen from the water.
† See also Chapter 3, page 33.
FISH AND RIVER POLLUTION

Table 35—cont.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Fish tested</th>
<th>Lethal concentration</th>
<th>Temp. °C</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>stickleback</td>
<td>13,000</td>
<td>17</td>
<td>6</td>
</tr>
<tr>
<td>Sodium sulphide</td>
<td>&quot;</td>
<td>4.5 S</td>
<td>17</td>
<td>7</td>
</tr>
<tr>
<td>Sodium sulphide</td>
<td>brown trout</td>
<td>1 S</td>
<td>17</td>
<td>18</td>
</tr>
<tr>
<td>Strontium chloride</td>
<td>goldfish</td>
<td>100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Strontium nitrate</td>
<td>stickleback</td>
<td>1,500 Sr</td>
<td>15-18</td>
<td>9</td>
</tr>
<tr>
<td>Sulphuric acid</td>
<td>goldfish</td>
<td>pH 3-9</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>&quot;</td>
<td>100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Tannic acid</td>
<td>trout alevins</td>
<td>&lt;100</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>Zinc (sulphate ?)</td>
<td>trout ova</td>
<td>0.01 Zn</td>
<td>7</td>
<td>7</td>
</tr>
<tr>
<td>Zinc sulphate</td>
<td>stickleback</td>
<td>0.5 Zn</td>
<td>14-17</td>
<td>1</td>
</tr>
<tr>
<td>&quot;</td>
<td>goldfish</td>
<td>&lt;1,000</td>
<td>18-23</td>
<td>1</td>
</tr>
<tr>
<td>&quot;</td>
<td>minnow</td>
<td>&lt;404</td>
<td>?</td>
<td>5</td>
</tr>
<tr>
<td>&quot;</td>
<td>rainbow trout</td>
<td>&lt;25 Zn</td>
<td>18</td>
<td>35</td>
</tr>
</tbody>
</table>

movements narrow vertical charts were used. The width of the chart represented the width of the tank and a time scale was marked off vertically, starting at the top. Equipped with stop-clock and pencil the observer would watch the fish and copy its movements to left or right by drawing a line on the chart.

The first substances to be tested were ammonia, ammonium salts, aniline, hydrogen sulphide, carbon bisulphide, phenol, cresols, naphthalene and a number of other constituents of the effluents from gas works. Most of the fish used were Notropis whipplii and Pimephales notatus, known in America as 'minnows', but thirteen other species were also tested. The general conclusion reached was that fish showed a very poor capacity for recognizing these substances. They would swim into the solution and then appeared to become intoxicated by it, so that thereafter they would avoid the water end of the apparatus. The chief defect of the gradient tank is the difficulty of avoiding vertical gradients of concentration. Wells discovered that with the supply running at the standard rate the solution was about six times as concentrated at the bottom as at the top. This is probably due to differences in density between water and solution supplies setting up a vertical stratification. Consequently it is very difficult to determine what concentration of the substance tested is encountered by the fish in its movements along the tank.

A considerable improvement is effected by redesigning the apparatus so that water and solution are sharply differentiated and do not mix to form a gradient. The basic arrangement used by the writer is shown in Figure 10.
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cylindrical glass container about 58 cm in length; water or solution can be delivered to the left side of this tube from the aspirators A or B; water or solution can be run in on the right from C or D. Two outlets are provided in the centre of the experiment tube leading to waste at H. The tube carrying the pinch-clip 3 serves for the expulsion of all air. With the water and solution running in at a suitable rate a very sharp vertical separation can be set up in the centre; this can be demonstrated by colouring one supply with dye. Modifications of this basic arrangement can be made to test the effect of deoxygenated water and solutions which decompose very rapidly 38, 39.

Figure 10. General scheme of apparatus for testing the reactions of fish to toxic solutions. A, B, C, D, 10 litre aspirators; E, F, bubble traps; 1, 2, 3, 4, 5, pinch clips; G, screw clip; G, position of outlets leading to waste at H. By courtesy of the Journal of Experimental Biology

The experiment is begun with water running in at both ends and then one water supply is replaced by the solution to be tested. Five or more fish can be used, their positions being spotted on the chart at 15 or 30 second intervals, or a single fish can be used, its movements copied on a vertical chart after the method of SHEL- 

FORD 40. Using a number of fish is quite successful if their movements remain more or less orderly but if the toxic substance tested induces wild swimming and other symptoms of intoxication it is better to use only one. To check the reactions displayed the direction of flow of water and solution can be reversed, or solution can
be run in on both sides for a time and then one solution supply can be replaced by water.

The results obtained with the various substances tested are strikingly different. We may consider first the reaction to lead nitrate; Figure 11 is a typical record for a 30 mm trout. The solution is 0·0001 N Pb(NO₃)₂—approximately 10 p.p.m. Pb. The fish is placed in the apparatus which is filled up from aspirator A (Figure 10) and water is run in on both sides. After 10–15 minutes

![Diagram](image)

**Figure 11.** Record of the reactions of a small trout to 0·0001 N lead nitrate. Temp. 18° C.

the fish has settled down and is moving normally. The stop-clock is now set at zero and the observer begins to record the movements of the trout on the chart. The animal keeps moving most of the time, traverses the tube twice. At 2 minutes the right-hand flow is replaced by lead solution and the fish goes to the other end. At about 4 minutes the trout swims up to the water-solution junction, as soon as it comes into contact with the lead nitrate it gobbles and retreats. Water is admitted on the right at 6 minutes, and at 7
minutes solution is run in on the left. Four times again the fish swims to the middle of the tube, stops, gobbles and retires. At 10 minutes water is once more set flowing through the left and the fish soon ventures into this side of the apparatus. This experiment is typical; fish seem to have a very good capacity for detecting and turning away from lead solutions. Sticklebacks avoid low concentrations very well but strong lead nitrate appears to intoxicate them. Minnows are very sensitive and soon detect and avoid a 0·00001N solution (1 p.p.m. Pb). Sticklebacks will also develop an avoiding reaction to dilute solutions of zinc sulphate. In about 20 minutes they seem to discover that it is best to stay out of 0·001N \( \text{ZnSO}_4 \), in which they live for about 7 hours in a survival time experiment. This concentration of zinc sulphate is quite devoid of taste, even if held in the mouth for some time.

Other substances which minnows and sticklebacks avoid quite successfully are sulphides, acids and alkalis. Sticklebacks retreat from water more acid than pH 5·4 or more alkaline than pH 11·4. They are therefore much more tolerant of alkalinity than acidity. To water of hydrogen ion concentrations between these limits they may show a vague positive reaction, a vague negative reaction or they may be quite indifferent. There are other substances to which a less successful avoiding reaction is displayed. Mercuric chloride is one of these and of the fish used in reaction experiments with this salt a high proportion die. The results with ammonia are interesting in that sticklebacks avoid comparatively high concentrations (0·04N, 0·01N) but seem to be attracted into low concentrations (0·001N).

The behaviour of the fish towards solutions of copper salts is surprising. A rather indefinite avoiding tendency is displayed at high concentrations (0·04-0·1N), but at greater dilutions (0·01 or 0·001N \( \text{CuSO}_4 \)) all signs of recognition of the toxic solution disappear and the fish congregate at the solution end of the apparatus where, sooner or later, they die. This 'positive' reaction seems to be produced in the following way: the fish are excited at first but they are quite incapable of detecting the copper sulphate, sooner or later when they chance to swim into it they tend to become stupefied and rest motionless on the bottom of the tube. If they revive and start to move about they may cross to the water end of the apparatus; here they appear to be stimulated and keep up aimless and erratic movements which eventually land them back in the solution where another period of stupor results. (See Figure 12.) Thus a toxic solution which is not 'recognized' acts as a kind of trap.

A further type of reaction is seen when we carry out the experiments with substances which seem to affect the animal's nervous
system and act as intoxicants. Figure 13 is a record for 0.02 per cent aniline and a single 30 mm trout. When the aniline solution is admitted the fish ventures into it five times becoming more and more excited, then it suddenly swims furiously up and down the tube finishing up upside-down in the solution. Water is admitted on the right at 5½ minutes; at 7 minutes the fish recovers its equilibrium and a minute or two later appears quite normal. A long series of experiments with minnows using various concentrations of phenol, ortho-cresol and para-cresol has given generally similar results. The fish have little or no capability of detecting and avoiding most concentrations of these substances into which they venture; then they very quickly lose their sense of balance and power of co-ordinated movement and swim about wildly until they collapse. At certain concentrations ortho- and para-cresol seem to have such an irritating effect that the fish may avoid the solution
ASPECTS OF RIVER POLLUTION

successfully but the conditions are critical. The time taken by the fish to establish an avoiding reaction is very little less than the time the solution takes to destroy its capability of doing so. It would seem that the irritant action of phenolic substances, which may repel fish, is distinct from their intoxicating effect, which renders the fish incapable of rejecting them, just as very strong alcohol has a local action and effect when taken into the mouth which is distinct from the intoxicating effect it produces when it reaches a man’s nervous system. Some typical records for minnows and para­cresol solutions are shown in Figure 14; at 0·03 per cent a good avoiding action is displayed, at 0·01 per cent the fish keeps venturing into the danger zone and at 5½ minutes becomes intoxicated.

Figure 13. The reactions of a small trout to 0·2 per cent aniline. Temp. 18° C

There is some evidence that under natural conditions fish will detect and avoid water of abnormally low oxygen tension. It has been stated that fish have never been seen killed outright by sewage­polluted water unless they are trapped and cannot get away. SHELFORD and ALLE42, some years ago, used the gradient tank to test the reactions of a number of American species to gradients of dissolved atmospheric gases. They concluded that there was little or no response to a nitrogen gradient and that the concentration of this gas is of no importance; that fish reacted negatively to carbon
Figure 14. The reactions of metalas to 0.03 per cent (two records), 0.01 per cent and 0.003 per cent para- crinal. pH of water and solutions 6.8. Temp. 15.5-18°C. By courtesy of the Journal of Experimental Biology.
dioxide or a deficiency of oxygen, indicating their dislike by moving away, rising to the surface and ‘coughing’ (i.e. making sudden, convulsive respiratory movements). These experiments, however, did not indicate how their behaviour is influenced by changes of temperature and by the actual concentrations of oxygen encountered.

Using an apparatus essentially similar to that designed for the tests with lead salts, sulphides and phenolic substances, the writer has carried out about 100 experiments to test the reactions of minnows, sticklebacks and trout fry to water of low oxygen concentration at temperatures from 3–24°C. At 3° sticklebacks take some minutes to react to water containing as little as 0·3 mg/l. Eventually the amplitude of the respiratory movements begins to increase and a pronounced dyspnoea gradually comes on. The fish suddenly starts to swim; when it finds its way into the well oxygenated water at the other end of the apparatus it seems to ‘breathe more freely’ at once and rests motionless. At 13° sticklebacks are much more active but there seems to be no immediate appreciation of the poorly oxygenated water. The fish will swim into it without any hesitation; they may then swim out again without fuss; they may leave and revisit this end of the apparatus several times. If they spend more than a certain minimum time in this half of the tube they suddenly develop a severe dyspnoea accompanied by an increase in the tendency to random swimming. This erratic movement sooner or later leads them out of the low-oxygen zone into the well aerated water where the respiratory distress subsides, the stimulus to swimming disappears and for a little while the fish stops still.

Minnows and trout fry behave like the sticklebacks at low temperatures and the general conclusion to be drawn from these experiments is that fish have no innate instinctive ability to recognize water of abnormally low oxygen tension; that they swim into it without hesitation or remain in it should it flow over them, provided that immediate and acute respiratory distress is not developed; that should they eventually avoid it the basis of the reaction is the active random movement incited by dyspnoea.

At higher temperatures, however, dyspnoea will come on much more quickly. At about 13° C trout fry or minnows will venture a little way into poorly oxygenated water and make a hurried retreat. At 20–24° C dyspnoea develops so rapidly that the fish generally avoid poorly oxygenated water almost immediately. A fish swimming up to the junction of the two supplies stuggers, coughs and swims backwards as if irritated or turns away (Figure 15).

Whether a fish turns back from water of low oxygen tension thus depends on the speed at which respiratory distress is developed,
this in turn depending on the degree of oxygen deficiency and the temperature.

Enough has been written in this chapter to show that the effects of pollution on fish is an interesting and complex problem. Emphasis has been laid on experimental work in the laboratory. Field observations are also necessary and their importance is not underestimated, but only experimental work can tell us exactly how polluting substances kill fish, whether their toxic action is one involving permanent damage after which the animal must die sooner or later, or whether they produce a condition of narcosis from which it may recover if the pollution is temporary; what concentrations are dangerous and what dilutions may be expected to be reasonably safe. New polluting substances present new problems. A number of new insecticides such as DDT, gam-

Figure 15. The reactions of trout fry to water containing 1.0 mg/l. of oxygen at 3°C; 1.5 mg/l. at 13°C; 0.56 and 3.0 mg/l. at 20°C. The figures opposite the large, tailed arrows indicate the oxygen content of the water running into the experiment tube. Figures opposite the small arrows are counts of the opercular movements (number per minute). By courtesy of the Journal of Experimental Biology.
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Figure 16. Lethal concentrations for some of the more important polluting substances. This figure is intended to give some idea of their relative toxicity, the range of concentrations involved and the relative sensitivity of various fishes. Based on the data in Table 35.

Figure 17. pH values tolerated by various fishes. The alkaline range value for the stickleback represents the most alkaline water the fish will enter in reaction experiments. The other points represent limiting degrees of acidity or alkalinity which, according to different authorities, these fishes survive indefinitely or, at least, for many days. The figures are only applicable when an abnormal concentration of H or OH ions results from the presence of strong mineral acids or strong alkalies; they are not applicable in cases of pollution by acids with basic anions or conditions of abnormal alkalinity produced by carbonates, sulphides, ammonia, etc. Based on the data collected and reviewed by Doktorow and Katz.2
use as soap substitutes are a further example, and experiments with these substances are being carried out at the new D.S.I.R. Water Pollution Research Laboratories. Detergents are rather complex substances and it is not easy for the experimenter to get information as to their chemical identity. Sodium tetrapropylene benzene sulphonate is one of their basic ingredients and the lethal concentration limit for this is about 6 p.p.m.49.

Generally speaking these newer pollutants are not so important as those which have been more extensively studied and much experimental work remains to be done on pollution by metals, acids, cyanides, ammonia, phenolic substances and oxygen-reducing effluents. Much of the available data on lethal limits applies only to goldfish, sticklebacks or rainbow trout and more information regarding brown trout and salmon parr is needed. Fortunately the method of 'bio-assay' of pollutants is becoming increasingly well known; in Lagler’s book on freshwater fisheries50 it is presented as a classroom study programme. More experimental work is desirable on the extent to which the toxicity of polluting substances is influenced by temperature changes, how far the resistance of fish can increase as the result of acclimatization and how far their growth is retarded by sub-lethal degrees of pollution. Information on the relative resistance of different fish is also required, on the lines of the work by Wuhrmann27 who has published valuable data indicating the relative resistance of brown trout, rainbow trout, tench, perch, minnow and chub to ammonia, cyanides and phenol. The whole problem is made much more difficult by the complexity of many industrial effluents which may contain a number of different toxic substances with very different effects. Recent work tends to show that oxygen concentration is of supreme importance where fish are concerned; the toxicity of an effluent may depend, eventually, on the oxygen tension—fish can survive doses of toxic substances in well-aerated water that would be fatal when the oxygen supply is deficient51.

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CHAPTER II

BIOLOGICAL ASPECTS OF RIVER POLLUTION


(Biologist, Birmingham Tame and Rea District Drainage Board)

3rd Fisherman: Master, I marvel how the fishes live in the sea.
1st Fisherman: Why, as men do on land: the great eats out the little one.

SHAKESPEARE, ‘Pericles’, Act II, Sc. i

Although river pollution may be said to be caused by chemical or physical agencies, it is essentially a biological phenomenon. In the past attempts have been made to measure pollution in terms of purely biochemical, chemical and physical standards. The direct measure of pollution, however, is the effects the polluting substance has on the plant and animal life in the stream, although chemical analysis and biochemical and physical tests may be necessary to explain these effects. After years of chemical and physical testing of river waters the river boards are today experiencing difficulties in the setting of standards for effluents, and it will only be in the light of biological surveys and tests that these standards will eventually be successfully determined. A knowledge of the biological aspects of pollution is then not only of interest but essential to the study of the problems of river pollution.

BIOLOGY OF STREAM LIFE

In order to fully understand the biology of pollution it is first necessary to consider some biological principles of stream life. For the benefit of the non-biologist the next few pages briefly outline the naming and classification of plants and animals of streams together with their activities, inter-relationships and factors influencing their distribution.

Systematic nomenclature

In this work the use of scientific nomenclature is essential as in many cases there are no popular names for the organisms we shall meet. Where these do exist they often refer to several species or to different species in different counties. It is usual to refer to organisms by two names, first the generic name denoting the genus or
tribe and secondly the specific name by which it is distinguished from the other species of the genus, i.e. surname and christian name. Thus the fresh water shrimp is *Gammarus pulex* and its marine relative *Gammarus neglectus*. As yet it is not possible to identify the species of all forms of fresh water organisms; many flies, for example, although they can be identified in the imago or adult stage cannot be identified specifically in their aquatic stages.

The different genera may, however, be distinguished and are then referred to by the generic name only, e.g. *Chironomus* sp., or *Chironomus* spp. if the reference is to more than one species. Although the name of every genus is different the same specific name is sometimes found in different genera, for example the specific name *fluviatilis* meaning 'of rivers' occurs in *Ephydatia fluviatilis*, the river sponge; *Acanthias fluviatilis*, the river limpet; and *Astacus fluviatilis*, the crayfish.

During the course of evolution the many different forms of life we know today have diverged from common stock and thus any system of classification has its limitations. In practice, however, it is convenient to have such a system of classification as that outlined in Tables 36 and 37.

Apart from viruses, about which little is known in connection with stream work, bacteria are the smallest although one of the most important members of the stream community. They are classified on the morphology of the cell and, although microscopic and measured in microns (μ = 0.001 mm), they may form colonies of visible or macroscopic size, for example, zoogloeal masses or filaments, e.g. *Sphaerotilus natans* (sewage fungus) (Plate 1 a–c). The fungi although conventionally classified as plants are probably more closely related to the bacteria. Unlike plants they are unable to manufacture their own food and rely upon organic matter for their nutrition. They are usually filamentous and together with bacteria are most evident in organically polluted streams.

Protozoa, the microscopic one-celled animals, are mostly aquatic and are well represented in the stream fauna. The great diversity of their morphology allows them to be classified into fairly well-defined classes. Some are colonial and assume macroscopic size; *Carchesium* spp. (Plate V c), for example, form tassel-like growths in some polluted streams which are sometimes called 'sewage fungus'. This term is also applied to a collection of organisms forming similar growths of which few are true fungi. Two other primitive phyla, Porifera, the sponges, and Coelenterata which in the sea are represented by the jelly fish and corals, are poorly represented in fresh waters, the sponges by *Ephydatia fluviatilis* and the Coelenterata by *Hydra* spp. The phylum Platyhelminthes (flat worms), most
Plate I. Some microflores of stream beds:

(a) Sphacelotheca natans (x 1); (b) Sphacelotheca natans on Elodea (x 1); (c) Filaments of Sphacelotheca natans (x 140); (d) Diatoms and Desmids (x 70); (e) and (f) Frustules of Diatoms including Rhizosolenia curvata and Diatoma sp. (x 350); (g) Oedogonium (x 30); (h) Vegetation with germinating zoo spores (x 35); (i) Cladophora (x 15).

(Plate I (a), (b) and (e) reproduced by courtesy of H. A. Hawkes and S. H. Jenkins "Biological Principles in Sewage Purification", J. Inst. Sew. Purif., 3, 1951.)
Plate II. Freshwater Annelida. (a) Tubifex worms and cases [slightly enlarged] (reproduced by courtesy of H. A. Hawkes and S. H. Jenkins 'Biological Principles in Sewage Purification', J. Inst. Sew. Purif., 3, 1951); (b) Glossiphonia sp. [actual size 3-5 cm long]; (c) Glossiphonia leech (young) [actual size 2-0 cm long]

Plate III. Crustacea. (a) Cyclops female with egg sacs [actual size 2-5 mm]; (b) Cyclops male side view [actual size 2-5 mm]; (c) Asellus aquaticus [actual size 2-0 cm]; (d) Gammarus pulex [actual size 2-0 cm]
Plate IV. Insecta

(a) Dytiscid larva, Coleoptera [actual size 1.0 cm]; (b) Ephemera sp., Ephemeroptera [actual size 1.5 cm]; (c) Ephemerella, Ephemeroptera [actual size 1.5 cm]; (d) Ephemerella sp., Coleoptera [actual size 2.5 cm]; (e) Ephemera sp., Ephemeroptera [actual size 3.0 cm]; (f) Hydroporus sp., Trichoptera [actual size 3.0 cm]; (g) Limnephilus larva, Trichoptera [actual size 3.0 cm]; (h) Nymph sp., Plecoptera [actual size 3.5 cm]; (i) Zoropsis sp., Neuroptera [actual size 2.0 cm]; (j) Nemoura sp., Plecoptera [actual size 2.5 cm]
Plate V. Some members of the "sewage fungus" complex.

(a) Beggiosis alba (x 530). (Reproduced by courtesy of T. G. Tomlinson).
(b) Leptosira lactea (x 270). (Reproduced from Water Pollution Research Technical Paper No. 8, by courtesy of the Controller, H.M.S.O.).
(c) Carchesium (x 70). (Reproduced by courtesy of T. G. Tomlinson.)
Plate VI. Some indicator algae

(a) Stigeoclonium (× 40), (Reproduced by courtesy of H. A. Hawkes and S. H. Jenkins, "Biological Principles in Sewage Purification", J. Inst. Sew. Purif., 3, 1951); (b) Cladophora (× 10), (Reproduced by courtesy of H. A. Hawkes and S. H. Jenkins, "Biological Principles in Sewage Purification", J. Inst. Sew. Purif., 3, 1951); (c) Rhizosolenia curvata on Cladophora (× 200); (d) Coccomorpha placenta (× 1500)
Tabl. 36. A classification of stream flora

**Bacteria** (Schizomyces—fission fungi)

- **Eubacteriales**: Mostly flagellate and unicellular.
- **Spirillaceae**: Markedly spiral; flagella polar, e.g. *Spirillum*.
- **Pseudomonadaceae**: Rod shaped with long polar flagella, e.g. *Pseudomonas*.
- **Bacillaceae**: Non-sporing rod-shaped forms, e.g. *Bactrerium coli*, *Escherichia coli*.
- **Chlamydobacteriaceae**: Bacterium-like with mucous sheaths or stalks, and flagellated swimmers, e.g. *Sphaerotilus*.
- **Bacillaceae**: Rod shaped with endospores, e.g. *Bacillus*, *Clostridium*.
- **Coccaceae**: Radially symmetrical, usually non-motile, e.g. *Staphylococcus*.
- **Actinomycetales**: Filaments with impermanent branches.
- **Mycobacteriaceae**: Short filaments, e.g. *Mycobacterium*.

**Fungi** (Thallus simple, usually filamentous, devoid of chlorophyll, reproduction by spores)

- **Phycomycetes**: Non-septate filaments, e.g. *Leptosphaeria*, *Saprolegnia*.
- **Fungi Imperfecti**: Life cycle not fully known, e.g. *Fusarium*.

**Algae** (Primitive plants bearing pigments and reproducing by spores)

- **Cyanophyceae**: Blue-greens, e.g. *Oscillatoria*, *Chamaesiphon*.
- **Bacillariaceae**: Diatoms. Single celled siliceous frustules, e.g. *Coscinodiscus*.
- **Chlorophyceae**: Green Algae. Contain the pigment chlorophyll.
- **Volvocales**: Unicellular or colonial, e.g. *Chlamydomonas*, *Gonium*.
- **Chlorococcales**: Unicellular or colonial, vegetative cells non-motile, e.g. *Scenedesmus*.
- **Ulotrichales**: Septate filaments, plates or tubes, e.g. *Ulothrix*, *Mollistroma*, *Enstromophora*.
- **Cladochonales**: Filaments, usually branched, cells multinucleate, e.g. *Cladophora*.
- **Chaetocellales**: Filament with prostrate and projecting systems, e.g. *Stigeoclonium*.
- **Oedogoniales**: Filamentous, end of cells striated. *Oedogonium*.
- **Conjugales**: Elaborate chloroplasts, no motile spores.
- **Zygnemaceae—Filamentous, e.g. *Stigeoclonium*.
- **Rhodophyceae**: Red Algae, e.g. *Batrachospermum*.

**Bryophyta** (Liverworts and mosses)

**Angiosperms** (Flowering plants, e.g. *Potamogelon*)

Species of which are parasitic, are also represented by the free living planarians. The Nematoda, or round worms, have some members wholly freshwater, whilst others are parasitic, some stages of which occur in fresh water. The Rotifera or wheel animals are essentially fresh water animals; the Polyzoa or moss animals, however, are mostly marine and have few genera in freshwater, e.g. *Plumatella*. The Annelida or the true segmented worms, include the classes Oligochaeta, or worms having bristles or chaetae, and the Hirudinea or leeches. (Plate II.)
Table 37. A classification of stream fauna

Protozoa (Microscopic unicellular animals)

Rhizopoda: Move and ingest food by pseudopodia.
   Amoebina: No shell, e.g. Amoeba.
   Tentacula: With shell, e.g. Anodonta, Diffugia.
Flagellata: Move by flagella, e.g. Euglena, Bob.
Ciliophora: Move by cilia.
   Ciliata: Ciliated throughout life.
   Holotricha: Uniformly ciliated, e.g. Paramecium, Colpidium, Limopsis.
   Heterotricha: Fine cilia and tougher cilia in bands, e.g. Stentor.
   Hypotricha: Flattened ciliates having stiffer cilia ventrally as legs, e.g. Apteidium, Ephrahine.
   Peritricha: Bell-shaped bodies borne on stalks, e.g. Verticilia, Carvelium.
Suctoria: Not ciliated in adult form. Bear suckorial tentacles, e.g. Actinia.

Porifera (Sponges, e.g. Ephydalia)

Coeleterata (Having 2-layered body wall enclosing single body cavity, e.g. Hydra)

Platyhelminthes (Flat worms)

Cestoda: Tapeworms, e.g. Taenia.

Nematoda (Roundworms, non-segmented, e.g. Nematodes)

Rotifera (Wheel animals, e.g. Rotifer)

Polychaeta (Moss animals, e.g. Fluvatella)

Annelida (True segmented worms)

Oligochaeta: The earthworms and allies with chaetae or bristles.
   Tubificidae: Usually above 3 cm long and having red blood, e.g. Tubifex.
   Lumbricidae: Thin worms up to 8 cm long with dark red blood (2 chaetae per bundle), e.g. Lumbricus.
Enchytraeidae: Up to 2.5 cm long, whitish, bristles simple.
Naclidae: Some bristles cleft at tips, e.g. Nais.

Arthropoda (Segmented animals with exoskeleton, each segment having one pair jointed appendages one or more of which modified as jaws)

Crustacea: Aquatic with two pairs of antennae, at least three pairs of appendages as jaws.
   Branchiopoda: Trunk limbs, broad lobed and fringed with hairs, e.g. Daphnia.
   Ostracoda: Enclosed in bivalve carapace, e.g. Cypris.
   Copepoda: No carapace. Antennae enlarged, e.g. Cyclops.
Malacostraca: The larger members. Eyes stalked.
   Isopoda: Carapace absent—body flattened top to bottom, e.g. Asellus.
   Amphipoda: Carapace absent—body flattened laterally, e.g. Gammarus.
   Decapoda: 5 pairs of thoracic walking limbs, e.g. Astacus.
Insecta: Body divided into a head, thorax and abdomen. Normally two pairs of wings and three pairs of legs on thorax.
   Apterygota: Without wings. Collembola, e.g. Antarctia.
   Pterygota: With wings.
BIOLOGICAL ASPECTS OF RIVER POLLUTION

Table 37—cont.

Exopterygota: Wings developing externally, shortened life cycle. Eggs—
nymph—imago.
Plecoptera—Stone-flies, e.g. Perla.
Ephemeroptera—May-flies, e.g. Baetis, Ephemerella, Caenis, Olsoom.
Odonata—Dragon-flies.
Hemiptera—Bugs, e.g. Coenra, (Water Boatmen), Vala, (Water Cricket),
Syrph.
Endopterygota: Wings developing internally, full life cycle. Eggs—larvae
—nymph—imago.
Neuroptera—Alder-flies, e.g. Sialis.
Trichoptera—Caddis-flies, e.g. Hydropsyche.
Coleoptera—Beetles, e.g. Dytiscus, Holmis.
Diptera—2-winged flies, e.g. Chromomyia, Sonatlia, Eristalis.
Arachnida:
Hydracarina—water mites.
MOLLUSCA
Gastropoda: Snails and Limpets. Shells of one piece, e.g. Limnaea, Hydrobia.
Lamellibranchiata: Mussels. Shells having two valves, e.g. Siphonaria.
PISCES (Fishes).

The phylum Arthropoda is one of the most important groups in
a study of river life. Its members are characterized by possessing
an external skeleton and jointed limbs; they range in size from the
water fleas, Daphnia, to the crayfish, Astacus. Of the three classes
in this phylum the Crustacea are truly aquatic and are well repre­
sented in fresh water. This class is subdivided on the basis of
structure and arrangement of the appendages and on the presence
or absence of a posterior extension from the head known as the
thoracic shield or carapace. The Branchiopoda, which include
the Daphnia, have their trunk limbs broadly lobed and fringed with
hairs. The Ostracoda, e.g. Cypris, are enclosed in a bivalve kidney­
shaped carapace whilst the Copepoda such as Cyclops (Plate III,
a and b) have no carapace. The larger Crustacea belong to the
sub-class Malacostraca and have stalked eyes. Within this sub-
class are three families: (i) Isopoda, in which the body is flattened
dorsal-ventrally, e.g. Asellus aquaticus (the water hog-louse) (Plate
III c); (ii) Amphipoda, with the body laterally compressed, e.g.
Gammarus pulex (the freshwater shrimp) (Plate III d); and (iii) Dea­
poda, which possess five pairs of walking limbs, e.g. Astacus fluviatilis
(the crayfish).

The second class in the phylum, the Insecta (Plate IV, a-h), are
characterized by the possession of three pairs of true legs and usually
one or two pairs of wings. Some orders such as the Neuroptera
(alder-flies), Trichoptera (caddis-flies) and Coleoptera (beetles)
have, like the Diptera or true flies, young or larvae which are quite
unlike the adults or imago. These larvae are the active feeding
and growing stage and before assuming the form of the imago they
enter into a quiescent stage, the pupa, in which metamorphosis
takes place. In other orders such as the Ephemeroptera (mayflies), Plecoptera (stone-flies), Odonata (dragon-flies and damselflies) and Hemiptera (water bugs), the young stages resemble the imago and have wings which develop externally; these are known as nymphs and develop without pupation into the imago, although in some cases such as the Ephemeroptera an imperfect adult or sub-imago is first formed. The Plecoptera, Odonata, Ephemeroptera and Trichoptera all have aquatic nympha! or larval stages but the imagines are aerial. The aquatic members of the Hemiptera, however, and some of the Coleoptera are truly aquatic in all stages the imago seldom leaving the water. Of the Diptera several families have aquatic larvae, the most important being the Culicidae (mosquitoes), Chironomidae (midges) and Simuliidae (black gnats), all of which are aerial in their adult stage.

Of the phylum Mollusca, two classes are represented in fresh water: the Gastropoda (snails and limpets) have a shell of one piece and the Lamellibranchiata (cockles and mussels) have shells with two hinged valves and plate-like gills. The vertebrata, or animals with backbones are represented mostly by the fishes. It is also the more primitive forms of plant life that are commonly represented in the river flora. The Algae are a diverse group of simple plants. Some, e.g. Chlamydomonas are one-celled and capable of locomotion, others both unicellular and multicellular, may, in their life cycle, form such motile one-celled stages. Some families have no such motile stages, e.g. Conjugales, which include filamentous forms like Spirogyra and Desmids. The Diatoms have frustules of silica and the characteristic shapes and markings of these are used in identification (Plate I, d-f). Apart from filaments, elaboration of the single-celled types has resulted in colonial forms in rows, (e.g. Scenedesmus), plates (e.g. Pediastrum), or spheres (e.g. Gonium). Of the filamentous forms some are unbranched rows of cells (e.g. Ulithrix) whilst others, e.g. Stigeoclonium (Plate VI a) are branched, others are non-septate, e.g. Vaucheria (Plate I k). Further elaboration of the thallus is found in Enteromorpha which is a tubular sheet, or the sheet like thallus of Monostroma which resembles the seaweeds. The Bryophyta, including the mosses and liverworts, are associated with moist habitats and some are found on the rocks in shallow stretches of streams. The flowering plants, Angiosperms, have several species associated with rivers; some such as the reeds are usually confined to the banks, others, however, are either floating like water lilies or submerged, e.g. Potamogeton spp.

Ecology

Having outlined the way in which plants and animals are classified systematically, we shall now consider their activities and
interrelationships in the river community. Animals and plants, generally speaking, differ from one another in their method of nutrition. Plants are capable of utilizing the energy derived from sunlight to synthesize food materials such as carbohydrates and proteins from carbon dioxide, water and simple inorganic salts, by the process of photosynthesis; they are said to be autotrophic. Animals are incapable of synthesizing their food and eat plants or other animals and are said to be heterotrophic. The solid residues produced by the death and waste products of animals and plants are known collectively as detritus. Complex organic matter both in solution and solid must be broken down to simple inorganic salts before it is again available to the green plant. This is brought about by the activity of micro-organisms which obtain their energy by the oxidation of this complex organic matter. Proteins, for example, are broken down to ammonium compounds by a series of heterotrophic bacteria which require complex organic material as food. Autotrophic bacteria, which are able to live on inorganic material, continue the oxidation. Nitrosomonas obtains its energy by the oxidation of ammonium compounds to nitrates which are in turn oxidized to nitrates by Nitrobacter. These two organisms are only active in the presence of oxygen and although able to carry on their activities in the presence of complex organic matter they are inhibited by certain amino-acids. Some bacteria, on the other hand, are only active in anaerobic conditions, i.e. in the absence of oxygen. In anaerobic muds of stream beds such bacteria break down cellulose, fats and proteins to such simple compounds as acetic acid, these are then attacked by another group of anaerobic bacteria, the methane-producing bacteria. Of these, Methanosarcina methanica, Methanosarcina mazei, Methanobacterium sohagenii and M. omelianskii are probably the most important.

Other organisms besides bacteria play an important role in this breakdown process. Fungi are directly involved in organic decomposition and are especially concerned with the breakdown of cellulose. Many Protozoa are saprozoic and obtain their energy by the breakdown of decaying organic matter, others are holozoic and live on bacteria which are thereby kept in a young active state. Protozoa are likewise kept in check by their predators such as the Rotifers. The solid detritus is also worked over by a group of organisms known as scavengers which obtain their food from such matter and by so doing assist in its stabilization. Many organisms such as insects and several Nematodes have in the past been considered as detritus feeders whereas they probably obtain their nutrition from the saprophytic micro-organisms. Similar saprobic growths developing in sewage filters are grazed by a number of organisms including dipterous fly larvae and worms. Figure 18 shows, in a
simplified diagrammatic manner, this food cycle. In rivers the cycle is complicated by the continuous loss of nutrient material and organisms due to the current, but to some extent the loss is compensated for by the gain from land drainage. The effect of the discharge of excessive amounts of nutrient organic matter is discussed later. Within this general food cycle are several food chains by which food in the form of small organisms is built up into successively larger animals. There is little available knowledge on food chains in rivers though a general example may be: Bacteria→Ciliate Protozoa→Rotifers→Chironomid larvae→leeches→fish.

![Diagram of food cycle in streams](image)

The organisms in any community are therefore interdependent and exist in a dynamic state of balance in which the populations, although constantly striving to increase, are maintained at a fluctuating level determined by their food supply and predators. Besides food, animals require oxygen for respiration and also as a result of this process they liberate carbon dioxide. Some animals of streams are able to use atmospheric oxygen; the mosquito larvae and the rat-tailed maggot, *Eristalis tenax* (see Figure 22, 2), have breathing tubes which communicate with the atmosphere, the diving beetles carry their air supply in the form of a bubble below their elytra in a similar fashion to the modern naval frogman. Most aquatic animals, however, depend upon the oxygen dissolved in the water. This oxygen is dissolved in the stream water by physical aeration especially in rapid stretches and from the photosynthetic activity of plants, especially algae. Photosynthesis is dependent upon light.
and although during the day the oxygen produced may exceed the respiratory requirements of the plants and animals, during the dark hours their need may deplete the oxygen in the water. Thus in a stretch of river with luxuriant vegetation, conditions of oxygen saturation during the day may during the night be replaced by a marked depletion in oxygen. Such diurnal variations have been demonstrated in the rivers Lark and Itchen. 

Apart from those organisms which are independent of the oxygen dissolved in the water, certain organisms such as tubificid worms, some chironomid larvae and *Asellus aquaticus* are capable of living in waters of low dissolved oxygen content. Others, however, such as the may-fly nymphs, stone-flies and *Gammarus pulex* require relatively high dissolved oxygen concentrations.

The distribution of the different animals and plants in streams is determined by environmental conditions. Of these the physical and chemical nature of the water, the rate of flow and the nature of the stream bed are probably the most important. Apart from pollution, which is discussed later, the calcium content of the water is the most important of the chemical factors influencing the nature of the stream life. *Gammarus pulex* and many molluscs which are abundant in hard water rivers such as the Skerne, Itchen and Lark are less frequent in the soft waters of the Tees and Cardiganshire rivers, which are richer in insect life.

The nature of the stream bed although affected by the rate of flow cannot always be directly related to it. A similarly rapid current may, for example, pass over a relatively unstable gravel bed or stable rocks depending upon the geological nature of the district. As these physical conditions may vary considerably in any one river we find therein several different associations or communities. Carpenter adopting the Continental system, divided rivers into four zones according to the dominant fish species: in the upper reaches or head streams the volume of water is small, the course inconstant and the temperature uniformly low. These head streams join to form the trout becks of more constant flow having a strong current passing over a rocky bottom. Lower down where the current is less rapid allowing vegetation to become established the typical minnow reach is to be found. In the lowland course the current is slow and the bottom muddy and thick vegetation may develop especially in the backwaters. Here there are large variations in temperature and dissolved oxygen. Not all rivers possess these four reaches and Butcher classified whole rivers on the basis of the nature of their source, i.e. whether from hills or mountains, springs and land drains, or low-lying marsh or fenland.

Besides listing the typical fish, Carpenter also lists other organisms found in the different zones. Unlike fish, however, most other
organisms, especially in the more rapid stretches, are bottom
dwellers and are restricted to their immediate habitat. It is im-
portant to realize that this may vary within any one zone and even
across the breadth of a stream, thus the plant and animal associa-
tions should for our purpose be considered in relation to the local
environment rather than to the general characters of the zone.
PERCIVAL and WHITEHEAD found that both the nature of the fauna
and the density of the population were closely related to the nature
of the stream bed. The size of stone, its resistance to disturbance
by current and the amount of vegetation were important factors.
Certain animals such as the may-flies Rithrogena and Ecdyonurus,
which cling to the larger stones, were more abundant in the rapid
reaches on stones with no visible vegetation. Their mode of life
is not favoured by growths of Cladophora or moss which instead
harbour such forms as Camis, chironomids and Nais. The density
of organisms was found to be much greater when vegetation was
present, the fauna being dominated by chironomids and Nais
although Baeti, Ephemerella, Gammarus, Hydropsyche and Helmis were
frequent.

POLLUTION AS A BIOLOGICAL PHENOMENON

From the outline given of the biology of streams it will be seen that
the plants and animals naturally exist in complex communities in
a state of dynamic balance. One cannot expect a stable equili-

brium to be established because there are so many varying factors
which affect the abundance of any particular member of the com-
munity. The nature of these communities is largely determined by
three interrelated factors: (i) Physical and chemical nature of the
water, (ii) Nature of the stream bed, and (iii) Current. Pollution
may be said to occur when the discharge of a substance into a stream
alters appreciably the composition or distribution of these com-
munities by changing any of the above mentioned factors. The
discharge of directly toxic material reduces both the number of
individuals and the number of species. Any substance which
although inert and non-toxic so changes the physical nature of the
stream bed as to alter the community must be considered a pollu-
tant. If the physical nature of a discharge, such as its colour or
temperature, affects the physical nature of the river water, this also
may affect the communities and hence must also be considered as
pollution.

Just as oxidation of organic matter derived from animal and
vegetable wastes and remains takes place in the natural food cycles,
so in a similar way by the same process streams are able to deal
with a limited quantity of such materials from the land. In fact
because of continuous loss due to the current they depend upon this to maintain the basic food supplies of stream life.

The entry of larger quantities of organic matter, however, provides so much nutrient material that bacteria and other microorganisms rapidly increase in numbers. By their activities the complex organic matter is broken down, as previously described, to simple innocuous substances; carbohydrates, for example, to carbon dioxide and water, proteins to simple salts such as nitrates, phosphates and sulphates. In this process these organisms obtain their energy but in so doing they remove oxygen from the water. Because of the current this depletion in dissolved oxygen, known as the 'oxygen sag' (see Chapter 6, page 151), is most noticeable some distance below the discharge. As the organic matter is used up and the bacterial activity decreases the dissolved oxygen again gradually increases by a process of re-aeration due to absorption from the atmosphere and to the photosynthetic activity of the plants. This whole process of recovery is known as self-purification.

The degree and extent of this 'oxygen sag' depends upon the pollutional load in relation to the quality and volume of the receiving water. In cases of mild pollution the dissolved oxygen drop is only slight and the stream rapidly recovers. In cases of extreme pollution, however, the oxygen may be completely used up, in which case the aerobic bacteria responsible for the mineralization process described above are no longer active. Their place is taken by anaerobic bacteria which do not require dissolved oxygen but are capable of utilizing chemically combined oxygen to obtain their energy. These continue the breakdown process but some of the end-products such as organic acids, ammonia, methane and hydrogen sulphide are toxic or objectionable. There are still other bacteria which in the absence of oxygen utilize simple salts; thus nitrates are reduced either to nitrogen or to nitrites and then ammonia; sulphates are likewise reduced to sulphides and sulphur. In such conditions a process of demineralization takes place which is detrimental to normal stream life.

Besides organic matter in solution and colloidal matter, many effluents carry large quantities of suspended solids which are deposited on the bed of the streams. For instance, it is calculated that from one works alone the average weight of such matter discharged to the river during 1952 exceeded 10 tons dry weight per week. These blankets of sludge may undergo anaerobic decomposition even though the supernatant water contains oxygen. Such blankets of sludge may persist after the discharge has ceased and cause oxygen depletion downstream when disturbed by floods, etc. Sulphate-reducing bacteria are inhibited by traces of dissolved oxygen but this effect is only limited to the surface of the sludge.
Work on the Thames mud has shown that sulphides are never found in waters containing dissolved oxygen. Certain autotrophic sulphur bacteria are capable of oxidizing sulphides in the presence of oxygen to sulphur. Wheatland, however, has shown that in the Thames the oxidation of sulphides in water is due to chemical and not bacteriological activity. Deposition of solid matter on the stream bed also affects the vegetation, suppresses the photosynthetic activity and so delays the recovery of the dissolved oxygen.

The extent and degree of the oxygen sag is also affected by temperature. In the summer the higher temperatures increase bacterial activity and therefore the oxygen sag is greater. Self-purification, however, takes place more rapidly and hence, although the sag is deeper, it occurs over a shorter stretch of river than in the winter. Probably this seasonal effect is enhanced by the greater photosynthetic activity during the summer. Since also the oxygen is less soluble in water at higher temperatures, septic conditions are more likely to arise in the summer. In this connection it is usual to express the dissolved oxygen as a percentage of the saturation figure at that temperature; aquatic animals, however, are concerned with the amount of oxygen available.

The development of micro-organisms on the bed in organically enriched streams may produce macroscopic growths such as sewage fungus. Although these assist in the self-purification by utilizing the organic matter, a part of this is built up into more complex living organic matter. When these organisms die, either attached to the stream bed or after having been swept downstream, they form a secondary source of pollution. Sewage fungus itself is not known to be poisonous to aquatic life although on decaying it may produce toxic substances or anaerobic conditions on the stream bed. The growth of Sphaerotilus in Danish streams receiving ensilage juices has been shown by Rasmussen to be the cause of the non-development of trout eggs on the stream bed. Although to many anglers prolific growths of sewage fungus have become synonymous with pollution the removal or suppression of it does not diminish the pollution but only the evidence of it. To prevent such growths it is necessary to remove first their source of nutrient, i.e. the organic pollutant.

These micro-organisms, which thrive on the increased organic matter form the base of several food chains and thus the food supply for the higher organisms is increased. The effect of these grazing organisms may be beneficial in converting the complex organic matter into less complex faeces or humus. The depleted oxygen supply, however, limits the number of species which can at first make use of this increased food supply. In the absence of severe interspecific competition those animals which are left rapidly

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multiply and are often found in large numbers. As purification takes place and the dissolved oxygen increases, more species become established. In the recovery zone and repurified zone the increased mineral content of the water results in an increase in the plant life, especially algae. Other plants, however, are found more commonly in organically enriched waters, e.g. *Stigeoclonium tenue* and certain diatoms.

It is seen, then, that the capacity of streams for self-purification is dependent upon biological as well as physical and chemical condition. The manner in which the different organisms in the stream community are affected by pollution will now be studied by referring to specific surveys carried out in this country and in America.

**TOXIC AND PHYSICAL POLLUTION**

*Toxic pollution*

The classical examples of toxic pollution are the polluted Cardiganshire rivers which after years of lead mining in the district were found to be almost barren. Most of the mines had fallen into disuse by the end of the nineteenth century although a few were re-opened during the 1914-18 war, but these again closed down shortly after the end of the war. The accumulated dumps of debris, however, formed a continued potential source of pollution; the lead content of the river water being higher after heavy rains. In 1919 Dr. Kathleen Carpenter began a series of biological examinations on several such rivers including the Lower Rheidol and Lower Ystwyth. The vegetation was sparse with the exception of the algae *Batrachospermum* and *Sachitra* which often flourished. Up to May 1922 only 14 species of invertebrate animals were recorded from the Lower Rheidol. As shown in Table 38 all these were in the phylum Arthropoda, mostly insects. Mollusca, Trichoptera, malacostracan Crustacea, worms and leeches were all absent. In the most polluted zones immediately below the mines some organisms existed. These included *Tanytarsus nebulosus*, *Simulium latipes*, *Cloeon simile* and in the summer *Velia currens* and *Sigara minutissima*. During this period the estimated dissolved lead concentration of the river water was 0.2 to 0.5 p.p.m.

Between 1922 and 1923 after the cessation of mining activities and during which period the concentration of lead was often nil and never exceeded 0.1 p.p.m. even in times of flood, there was a noticeable improvement in the condition of the river. There was not only a marked increase in the number of species of fauna to 29 but also an increase in the numbers of individuals; species which were previously rare became abundant. This increase in species
which included Trichoptera, the Crustacean *Canthocamptus* and *Polypedilus nigra*, was associated with an increase in the vegetation; *Callitriche verna* (Starwort) and *Ranunculus aquatilus* (Water Crowfoot) appearing and the Algae and Bryophyta being considerably augmented. After a further period of recovery a survey carried out between July 1931 and May 1932 showed that the number of animal species had risen to 103 (Table 38) though some of these were only rare.


<table>
<thead>
<tr>
<th>Number of species recorded from Lower Rheidol</th>
<th>Prior to May 1922 (See Ref. 7)</th>
<th>May 1922 to March 1923 (See Ref. 7)</th>
<th>May 1932 to July 1932 (See Ref. 8)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platyhelminthes:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbellaria</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>Annelida:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oligochaeta</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>Hirudinea</td>
<td>0</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>Arthropoda:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Crustacea</td>
<td>3</td>
<td>4</td>
<td>1</td>
</tr>
<tr>
<td>Insecta:</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Plecoptera</td>
<td>2</td>
<td>2</td>
<td>8</td>
</tr>
<tr>
<td>Ephemeroptera</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Odonata</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Hemiptera</td>
<td>2</td>
<td>2</td>
<td>12</td>
</tr>
<tr>
<td>Neuroptera</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Trichoptera</td>
<td>0</td>
<td>8</td>
<td>17</td>
</tr>
<tr>
<td>Coleoptera</td>
<td>2</td>
<td>4</td>
<td>36</td>
</tr>
<tr>
<td>Diptera</td>
<td>1</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Mollusca</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Vertebrata</td>
<td>0</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Total number of species</td>
<td>14</td>
<td>29</td>
<td>103</td>
</tr>
<tr>
<td>Estimated concentration of dissolved lead in water</td>
<td>0.0-0.5 p.p.m. (see Ref. 7)</td>
<td>0.5 p.p.m.</td>
<td>Normal 0.0-0.2 p.p.m.</td>
</tr>
</tbody>
</table>

A comparison of the fauna of the Lower Rheidol with the lower reaches of the neighbouring unpolluted river Teifi showed that whereas the latter is populated by species typical of flowing waters, among the fauna recolonizing the Rheidol were species characteristic of static waters. This suggests that it was repopulated from
the numerous nearby pools, many of the colonizers belonging to the Odonata and Coleoptera characteristic of static waters whose powers of flight would facilitate this invasion. A still more recent survey listed 130 species from the mainstream, 97 of which were insects. It was considered that the fauna was not rich and this was probably due to the instability of the river bed and lack of submerged vegetation, although the absence of such forms as Gammarus pulex was due to the high acidity.

Studies on the neighbouring polluted river Ystwyth showed that before May 1922 it supported a similar fauna to the Rheidol and that immediately after the cessation of mining activities a parallel recovery in the fauna took place; green algae appeared and the numbers of species of animals increased from 9 to 26, 7 species of Trichoptera reappearing. This re-population of the river took place by the migration of larvae from some unpolluted tributary streams, as shown by the occurrence of large numbers of larvae at the confluence of tributary streams and the river and by the time of incursion in May before the imago appeared. A more recent survey, however, showed that the river had not then fully recovered; the fauna being limited to Insecta, Hydracarina and Platyhelminthes. The absence of fish, Mollusca, and malacostracan Crustacea was attributed to the continued pollution of the river by zinc derived from the disused lead mines. It was found that at normal flow although the lead concentration was 0·05 p.p.m., the zinc content was 0·7 to 1·2 p.p.m. Even in heavily polluted streams containing 60 p.p.m. of zinc in solution some insect larvae persisted, e.g. the stone-flies Leuctra sp. and Nemoura sp. A comparison of the fauna of the Ystwyth with that of the unpolluted Dovey showed that the latter contained 84 species not found in the Ystwyth; of these only 18 were known to be affected by the heavy metallic salts, the remainder were considered to be tolerant to metallic pollution. Their absence from the Ystwyth was considered to be due to the inhospitable physical nature of the river which on account of silting up was shallow, swift flowing and the stream bed unstable. The instability of the stream bed and the continued toxic nature of the water resulted in it being almost completely devoid of vegetation.

The general conclusion from these investigations is that pollution by heavy metals has the effect of reducing the number of species and the number of individuals. There is a marked gradation in the tolerance of different organisms. Fish are the most sensitive, being eliminated in water containing about 0·3 p.p.m. lead, at which concentration the invertebrate fauna is little affected. With increase in concentration, the fresh water limpet Ancylastrom fluviatile is eliminated, then other Mollusca and malacostracan Crustacea,
followed by Oligochaeta, Leeches and Trichoptera leaving a fauna restricted to certain insects, entomostracan Crustacea and some Planarians. In highly polluted waters containing 3 to 6 p.p.m. of lead the population is further restricted to the larvae of the midge Taxypus nebulator and the may-fly nymph Coleoptera similis. Laboratory toxicity tests showed that the survival times of different organisms agreed in general with these field observations.

Table 39. Effect of toxic discharges on flora and fauna of the rivers Churnet and Dove.
By courtesy of the Trent River Board (from Trent Fishery Board Report 1938)

<table>
<thead>
<tr>
<th>R. Churnet</th>
<th>Distance from Discharge miles</th>
<th>Number of Algae per mm²</th>
<th>Animals</th>
<th>Number of species</th>
<th>Number per unit area</th>
<th>Ca concn. p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above Frogshall</td>
<td>½ above</td>
<td>1,600</td>
<td>15</td>
<td>&gt;5,000</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Below Frogshall</td>
<td>1st discharge</td>
<td>150</td>
<td>0</td>
<td>0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Below Oakamoor</td>
<td>3</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>1.2 (1.6)</td>
<td></td>
</tr>
<tr>
<td>Alton Churnet</td>
<td>5</td>
<td>16,700</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>Mouth</td>
<td>11</td>
<td>50,200</td>
<td>2</td>
<td>2</td>
<td>0.6</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>R. Dove</th>
<th>Distance from Churnet mouth miles</th>
<th>Number of Algae per mm²</th>
<th>Animals</th>
<th>Number of species</th>
<th>Number per unit area</th>
<th>Ca concn. p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Above Churnet</td>
<td>Above</td>
<td>2,800</td>
<td>30</td>
<td>1,193</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Below Churnet</td>
<td>500 yd.</td>
<td>27,600</td>
<td>4</td>
<td>42</td>
<td>0.14</td>
<td></td>
</tr>
<tr>
<td>Deerbridge Mill</td>
<td>2</td>
<td>55</td>
<td>6</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sudbury Bridge</td>
<td>8</td>
<td>55,100</td>
<td>8</td>
<td>59</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>Sessayon Monk's Bridge</td>
<td>12</td>
<td>53,300</td>
<td>12</td>
<td>371</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>

A further example of the toxic effect of metal wastes is that of the pollution of the rivers Churnet and Dove by copper wastes. The river Churnet at the time of the investigation was in its upper reaches organically polluted by sewage effluent and dye works effluent which affected the fauna and flora in the manner described later. 7.5 miles downstream of these effluents the river had partially recovered, sewage fungus was rare, algae more common and the fauna abundant and varied. (Table 39.) The river then received a discharge from a copper works and the effect of this was to
elaborate the macrofauna and limit the numbers of algae. At this point 1 p.p.m. copper was found in the water and on one occasion below a second copper works three miles farther downstream a concentration of 1·6 p.p.m. was recorded. Five miles below the first discharge the algae had increased markedly but the species present were different from those found in the other parts of the river. A further 6 miles downstream where the Churnet enters the Dove there was a further increase in the amount of algae but animals were very rare. The abundant and varied fauna of the Dove above the Churnet was considerably reduced below the confluence and the diatoms were replaced by algae typical of the polluted stretch of the Churnet. This effect was still evident 19 miles downstream, that is 30 miles below the first discharge, although at this point there were signs of recovery, the copper concentration being 0·1 p.p.m.

The manner in which toxic materials affect animals differs with the animal and the ions concerned. Toxicity to fish is dealt with in the previous chapter. Jones14, using the planarian Polydora nigra and Gammarus pulex, investigated the toxicity of several metallic salts. He concluded that in the case of heavy metal salts the toxic effect at concentrations below isotonicity is due almost entirely to the cation, the toxicity of the anion being relatively small. At concentrations above isotonicity the anion and the osmotic pressure of the solution act as additional lethal factors. Salts of the alkalis and alkaline earth metals were shown to be comparatively harmless below isotonicity, with the exception of salts having a toxic anion such as chromate. The degree of toxicity of the hydrogen ion and 18 metals to Polydora nigra was assessed. On a p.p.m. basis their order of increasing toxicity was: Sr, Na, Ca, Mg, Mn²⁺, Pb, K⁺, Al, Co³⁺, Cr³⁺, N₃⁻, As³⁺, Zn, Cd²⁺, H, Au⁺³, Cu²⁺, Hg²⁺, Ag. The position of iron was uncertain, the toxicity of ferric solutions appearing to be due to their acidity. Barium salts gave irregular results. It was found that there was a decided relationship between the solution pressures of the metals and the degree of toxicity of their salts. This suggests that the degree of toxicity of ions is largely determined by the ease with which they form complex compounds with protoplasmic materials. The toxic action of heavy metal salts appears to be due to their action on the intracellular proteins resulting in a process of fixation. Other lethal effects are due to osmolyis in hypotonic solutions and the possible diffusion of ions into the body to alter the viscosity of the protoplasm. Excessive stimulation of the musculature with eventual disintegration was brought about by barium salts.

Anions although less toxic than the cations show a marked gradation in their degree of toxicity to different invertebrates. Jones15 using Polydora nigra as a test animal assessed the degree of toxicity
of 27 anions by determining in each case the molar concentration in which the animal survived for 48 hours at 15 to 18°C. The order of increasing toxicity was found to be:

ClO₃⁻ Cl⁻ Acetate CO₃⁻ Tartrate S₂O₃⁻ I⁻ PO₄⁻ Br⁻

CITRATE CO₃⁻ As₂O₃⁻ CrO₃⁻ IO₃⁻ F⁻ Fe(CN)₆⁻ NO₂⁻ NO₃⁻ CN⁻ S⁻ OH⁻

With cyanide the respiratory rate was heavily depressed but the survival time was three days or longer. Although the normal respiratory rate of *Polycelis nigra* (0.165 ml. of oxygen/g/h) is not much less than that for trout, *Polycelis* is considerably more resistant to cyanide; this is probably connected with its ability to survive many hours in waters with depleted oxygen supply. ANDERSON using *Daphnia magna* as his test animal and centrifuged lake Erie water as dilution water, tested the toxicity of 38 sodium salts. Of these, the chromate and dichromate were most toxic proving fatal at less than 1 p.p.m.; next came arsenite, perborate, cyanide, iodide and sulphide, all of which were toxic at less than 10 p.p.m. and the arsenate, nitrite and thiocyanate at less than 20 p.p.m.

All salts were found to be toxic when in high enough concentration to exert unfavourable osmotic pressures. Thus sodium acetate, bromide, chloride, formate and nitrate had approximately the same threshold concentration in terms of molarity, whilst sulphate and bicarbonate were innocuous except at concentrations of high osmotic pressure. Other salts may be toxic for different reasons; sulphate and bisulphite for example produce a low pH whilst the carbonate and hydroxide produce a high one.

Several of these inorganic poisons are present in wastes from different industrial processes such as cyanides from gas works, toxic metals from metal processing works, chromates from plating works, arsenic from tanneries and acids and alkalies in textile effluents. To these, new synthetic chemicals are constantly being added; the increasing manufacture and use of synthetic insecticides forms an added potential source of toxic pollution. The toxicity of synthetic detergents to fish and other freshwater life has been investigated. It was shown that at a concentration of 5 p.p.m. of the active component these were fatal to *Daphnia* after 10-100 hours. The full effect of the increasing discharge of these detergents on stream life is not yet fully known. Apart from toxic effects and the retarding of re-aeration, physical effects such as foaming and the decrease in surface tension may affect the life of those organisms which at some stage of their life cycle are concerned with the surface film, e.g. insects on emergence and egg laying.
In America, toxicity tests, using invertebrate animals such as *Daphnia*, are being developed for the routine testing of trade effluents. Although this is to be recommended, a full picture of the effect of such discharges is best obtained by examination of the stream fauna. Before applying the results of toxicity tests several complicating factors have to be considered. In the case of some toxic substances their effect varies with the dissolved oxygen concentration, being more toxic at lower concentrations of dissolved oxygen. Animals which can withstand low oxygen concentrations are usually less affected by these substances. Antagonism, whereby the toxicity of a substance is reduced when in the presence of a second substance, is a further complicating factor. Thus the addition of lead nitrate to a solution of copper nitrate reduced its toxicity to *Polypleis nigra*. Beyond a certain concentration of lead, however, 0-005N, this effect diminishes and at high lead concentrations the mixed solution is more toxic than the copper nitrate alone. Calcium is antagonistic to many metals including the toxic heavy metals making them less dangerous to the fauna in hard water streams than in soft waters. In other cases, however, the mixing of substances results in a mixture more toxic than their additive effect alone; this is known as synergy. Light may also affect the toxicity of substances to stream fauna. Investigations in 1930 on the effect of rain washings from tarred roads showed that they were not injurious to stream life except the first washings from recently tarred roads. The washings from roads which were breaking up were decidedly toxic. Naphthalene was the most toxic component and it was found to be more toxic in June than in February; this was attributable to temperature. More recently, however, Mottram, working on substances dissolved from the refined tar surfaces used today, showed that in the presence of sunlight these substances were toxic to many stream organisms. In evidence that this photosensitization effect was operative in streams he found that organisms which normally hide from light were not affected in streams where the others were reduced in numbers by tar wastes.

**Physical pollution**

A substance, although neither toxic nor putrescible, is still polluting if it so alters the physical nature of the water or of the stream bed to affect adversely the stream community. The effect of this type of pollution is often more lasting than either toxic or organic pollution. In the case of the River Ystwyth after partial recovery from lead pollution the absence of certain species was attributed to the silted unstable conditions of the stream bed which resulted from the mine workings. The entry of a textile mill effluent into the River Holme in West Yorkshire resulted in a marked reduction in the numbers of...
Only silt-loving forms such as *Nais*, *Tanytaspis*, snails and leeches were found below the discharge compared with a rich fauna, mostly insect larvae, found in the unpolluted stretches above. This was attributed not to any depletion in dissolved oxygen, but to the blanketing of the stream bed with a sludge containing textile fibres which prevented the growth of vegetation and thereby reduced the numbers of vegetable feeders. Other organisms such as *Trichoptera*, *Ephemeroptera*, *Simulium* and *Gammarus* which rely upon a flow of clear water for respiratory purposes were also adversely affected. Similar types of pollution may result from paper mills, quarrying and mining. The blanketing effect of humus solids in sewage effluents has already been mentioned. Again, the absence of life from many streams in Devon and Cornwall is attributed to the china clay wastes which are not toxic nor do they absorb oxygen from the water; sea trout, in fact, are reported to pass through the affected River Fal to spawn. This pollution results from the reduction of algal growths which form the basis of many food chains.

**ORGANIC POLLUTION**

The general effects of organic pollution on stream life have been established by several surveys. In this country most of these have been carried out by the Ministry of Agriculture and Fisheries; the results of some of these and of earlier work in America are outlined below.

*Middle Illinois river (1913-25)*

Between 1914 and 1920 growth and increased activity of contributory sources of pollution resulted in increased organic pollution of the Illinois river. Until 1920 sewage and wastes were discharged to the river with no treatment at all. Between 1920 and 1925, although the increase in population continued, sewage treatment and the treatment of the wastes from corn processing factories reduced the pollutional load. The corresponding changes in the bottom fauna were followed by a study of 1,308 biological collections taken over 225 miles between 1913 and 1925.

Deterioration in the river conditions between 1913 and 1920 resulted in a general reduction in the numbers of species represented in the bottom fauna (*Table 40*). A further indication of the increased pollution was shown by the disappearance of characteristically clean water species during this period followed by a slight recovery before 1925. Increasing pollution resulted in a decrease in the average numbers per square yard of stream bed of all groups except the Tubificids and Chironomids which increased enormously. *Table 40* shows the fluctuations in numbers of organisms per square
yard of different groups taken from a 10-mile stretch above Havana. Other important groups which declined were Odonata, Planarians, Amphipoda, and Ephemeroptera; these, unlike the Sphaeriidae, whose rapid recovery indicated unusual tolerance, were slow to re-establish after improvement in conditions. This delayed recovery of the bottom fauna compared with that of the dissolved oxygen, plankton and bacteria was considered to be due to two factors. Firstly, with the shortening of the polluted zone, the upstream respread of organisms from the lower unpolluted zone was slow compared with the downstream spread of pollutional types. Secondly, and probably the more important, was the reflooding of the river bed with incompletely oxidized organic solids from previous pollution.


<table>
<thead>
<tr>
<th>Year</th>
<th>Total number of samples</th>
<th>Number of clean water samples</th>
<th>Average number of organisms per yd.2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Citronomidae</td>
<td>Sphaeriidae</td>
</tr>
<tr>
<td>1915</td>
<td>21</td>
<td>12</td>
<td>1,709</td>
</tr>
<tr>
<td>1920</td>
<td>15</td>
<td>5</td>
<td>46</td>
</tr>
<tr>
<td>1924</td>
<td>21</td>
<td>0</td>
<td>12,785</td>
</tr>
<tr>
<td>1925</td>
<td>20</td>
<td>4</td>
<td>6,465</td>
</tr>
</tbody>
</table>

* Specimen: 1913-15

River Tees

A survey of the tidal and non-tidal reaches of the river Tees24, 25 showed the effect of sewage effluents and, in the case of the estuary, of industrial discharges on the flora and fauna of the river.

The river can be conveniently divided into the following three stretches, of which (i) and (ii) are non-tidal:

(i) A 55-mile stretch from the source at Cross Fell to Croft where it is joined by the river Skerne.

(ii) From Croft to Yarm a distance of 24 miles.

(iii) The 20 miles of the estuary between Yarm and the sea.

Above Croft the river was rapid with a bed of stone and rock which, except for a slow-flowing 3-mile stretch above Cauldron Snout known as the Weel, supported little rooted vegetation. Although this upper stretch received effluents from small sewage works the quantity was small and the dilution great, with the result
that the pollutional effects were only local. Immediately below these discharges, however, a change in the sessile microflora was observed. In the non-polluted stretch above Middleton-in-Teesdale the algal community was dominated by the diatoms *Achnanthes* spp. together with *Chaetopeltis* in the summer. Below the effluents this community was replaced by one in which *Cocconeis* and *Chamae­siphonopsis* were dominant. The entry of these discharges did not seriously alter the nature of the macrofauna communities but quantitative collections showed that the common animals, especially the Chironomids, were more numerous below; *Limnaea pereger* was also associated with the entry of sewage effluents.

In contrast to these small sources of pollution, the entry of the polluted River Skerne at Croft produced some marked changes in the flora and fauna. However, other changes affecting the biology of the river took place; viz. below Croft the river bed was more stable and the flow less rapid; the Skerne besides increasing the organic matter also raised the calcium content. These factors resulted in an increase in the rooted vegetation, thereby increasing the total number of animals. Some of the changes in the flora and fauna, however, are attributable to the increase in pollution by the Skerne. Silting, due to sewage effluents, resulted in the establishment of a silted macroflora community dominated by *Potamogeton interruptus*. The microflora which in the unpolluted stretches above Croft was dominated by the *Achnanthes-Chaetopeltis* community was below Croft replaced by *Cocconeis, Navicula viridis, Nitzschia pales* and *Stigeoclonium*. The abundance of *Cladophora glomerata* or blanket weed, and *Sphaerotilus* below Croft was also shown to be due to pollution. Above Croft these growths were only found associated with sewage effluents. The changes in the macrofauna are shown in Table 41. Some changes such as the occurrence of *Simulium equinum* and *S. reptans* were attributed to the increased vegetation below the Skerne; other changes, however, must have been due to an increase in organic matter and a decrease in oxygen. The serious effects of pollution on the fauna were limited to a short stretch of the river. Immediately below the entry of the Skerne Tubificids were the dominant organism, but only 200 yd. downstream they decreased, whereas the numbers of *Limnaea pereger, Ancylastrium fluviatile, Asellus aquaticus*, and *Erpobdella octoculata* increased. Downstream these, except *Erpobdella octoculata*, also decreased giving way, 650 yards below the Skerne, to a community containing organisms normally found above Croft. The Skerne itself although polluted near its source recovered in its middle reaches but was again seriously polluted by discharges at Darlington and finally by the Darlington sewage effluent just before its junction with the Tees. *Cladophora* was abundant in the middle
reaches and the diatom *Rhizosiphon curvata*, which was only found occasionally in the Tees, was common. Although little sewage fungus was present above Darlington, below it was abundant and extended down into the Tees below Croft. The extent of this growth downstream varied seasonally, being more extensive in the winter when self-purification was slower. In the polluted upper reaches only a few chironomid larvae and Tubificids were found. Downstream, however, chironomid larvae, *Simulium ornatum* and


<table>
<thead>
<tr>
<th>Distance from Skerne mouth (yd.)</th>
<th>100 above</th>
<th>100 below</th>
<th>300 below</th>
<th>400 below</th>
<th>500 below</th>
<th>600 below</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total number of organisms in 2500 cm² of river bed</td>
<td>7</td>
<td>107</td>
<td>214</td>
<td>93</td>
<td>131</td>
<td>90</td>
</tr>
<tr>
<td>Percentage composition</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chironomidae</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichoptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydropsychidae</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ephemeroptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coleoptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Heteroptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mollusca</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oligochaeta</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hirudinea</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrozoa</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Hydropsychidae* sp. were common. Still farther downstream, *Batis* and *Limnaea* appeared and in the middle reaches, the purest zone, the dominant organisms were *Hydropsyche sp.*, *Hydrobia sp.*, Battis sp., *Gammarus pulex*, and *Hydrobia jenkinsii*. Below Darlington successive pollutions resulted in a progressive deterioration in the fauna. *Batis* was reduced and *Anisus aquaticus* and *Sphaerium* increased in numbers. *Hydropsyche sp.*, *Gammarus pulex*, and *Hydrobia jenkinsii* disappeared and others except the Chironomids and Tubificids were few. Below Darlington sewage effluent, only Chironomids and Tubificids remained.
The estuary of the Tees, unlike the fresh water stretches, was grossly polluted. In a stretch of about seven miles below Stockton crude sewage and numerous industrial effluents, including tar acids and cyanides, were discharged to the river. Because of the long retention period in the estuary during which time the water passes up and down at each flood and ebb of the tide, considerable deoxygenation took place, especially in the hot summer months.

At the mouth of the estuary the marine flora and fauna were varied and abundant. As the estuary was ascended, however, there was a rapid decrease in the numbers of species. In the central portion few species of animals or plants were found; at Newton, nine miles upstream, only two species of animals were found, *Gammarus duebeni* and the rag-worm *Nereis diversicolor*, and the algae *Enteromorpha compressa*, *Oedogonium sp.*, *Closterium sp.*, *Fucus vesiculosus* (the common Bladderwrack) and *Pilayella littoralis*. Above this zone, fresh-water species gradually increased until at Yarm an abundant and varied freshwater flora and fauna were found. In the Tees this dearth of species in the middle estuary coincided with the zone of maximum pollution. Examination of unpolluted estuaries such as the Tay showed, however, that there was a similar reduction in species in the middle reaches although in the unpolluted estuaries the marine species penetrated into waters of lower salinity than they did in the Tees. It appears that the dearth of species in the middle reaches of estuaries is due to the inability of marine or fresh-water species to withstand salinity variations. The effect of pollution in the Tees is to further restrict the extent of invasion of the less saline waters by marine organisms. (Figure 19.) Work on the Mersey estuary has shown that there the distribution of species was similar to that in the Tees and Tay except that, because of the high speed of the tidal currents, the large amount of sediment in the water and the relatively small area of tidal banks, only half the number of species recorded from Liverpool Bay were found in the Narrows, the narrow stretch at the landward end of the Bay, although the salinity was the same.

**River Trent**

The effect of pollution and repurification on the flora and fauna of the Trent has been reported by Butcher. The upper Trent receives pollution from the Pottery towns via the Fowlea brook at Stoke. Table 42 shows the changes in the dominance of certain organisms throughout the 35 miles stretch below this pollution. In the first five miles of foul pollution the numbers and species of animals were few, sewage fungus was abundant, and the numbers of algae low, whilst certain species common above were absent. At the downstream end of this zone *Stigeoclonium* was abundant. The
first stage in the recovery was indicated by the increase in numbers of Tubificids and Chironomids 8 to 17 miles below Stoke. A decline in these and an increase in Asellus characterized the zone of mild pollution as far as Rugeley and a further 7 miles downstream. In the repurified zone below Rugeley a further increase in the numbers and variety of algae occurred, sewage fungus was absent and the fauna more varied.

Figure 10. Comparison of the percentage saturation of dissolved oxygen and percentage numbers of species along the Tees and Tay estuaries

The River Tame, a major tributary of the Trent, is heavily polluted near its source in the Black Country. A biological examination in 1940 showed that there was a similar succession (Table 43) of animals and plants as in the Trent itself. The repurification of the Tame, however, was considerably slower; the zone of mild pollution with Asellus as the dominant animal and the Nitrosaca palus and Comophona community of the algae common, which in the Trent appeared 20 miles below serious pollution, did not appear in the Tame before it had joined the Trent over 40 miles from its source.
Table 42. Effect of pollution on the distribution of organisms in the river Trent (1939-7). Reproduced with permission from R. W. Butcher, by courtesy of the Institute of Sewage Purification.

<table>
<thead>
<tr>
<th>Station</th>
<th>Mites from Foetus Bract</th>
<th>Fauna</th>
<th>Algae No. (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Firstfield</td>
<td>Gasteropods</td>
<td>Lamellibranchia</td>
</tr>
<tr>
<td>Milton</td>
<td>2</td>
<td>5</td>
<td>130</td>
</tr>
<tr>
<td>Trentham</td>
<td>2</td>
<td>4</td>
<td>15</td>
</tr>
<tr>
<td>Strongford</td>
<td>5</td>
<td>7</td>
<td>680</td>
</tr>
<tr>
<td>Tittensor</td>
<td>5</td>
<td>No collection</td>
<td>1,620</td>
</tr>
<tr>
<td>Stone</td>
<td>6</td>
<td>7</td>
<td>620</td>
</tr>
<tr>
<td>Aston</td>
<td>10</td>
<td>12</td>
<td>620</td>
</tr>
<tr>
<td>Sandon</td>
<td>12</td>
<td>24</td>
<td>670</td>
</tr>
<tr>
<td>Ingestre</td>
<td>17</td>
<td>7</td>
<td>36</td>
</tr>
<tr>
<td>Wolseley</td>
<td>22</td>
<td>2</td>
<td>54</td>
</tr>
<tr>
<td>Rugeley</td>
<td>24</td>
<td>1</td>
<td>75</td>
</tr>
<tr>
<td>Handsacre</td>
<td>27</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td>Yoxall</td>
<td>30</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Wichnor</td>
<td>35</td>
<td>11</td>
<td>7</td>
</tr>
</tbody>
</table>

Table 43. Effect of pollution on distribution of organisms in river Tame (1940-6). Reproduced with permission from R. W. Butcher, by courtesy of the Institute of Sewage Purification.

<table>
<thead>
<tr>
<th>Station</th>
<th>Mites from River</th>
<th>Fauna</th>
<th>Microflora No. (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Slimevibion</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Newton Green</td>
<td>5</td>
<td>68</td>
<td>100</td>
</tr>
<tr>
<td>Perry Barr</td>
<td>10</td>
<td>93</td>
<td>60</td>
</tr>
<tr>
<td>Sailford Bridge</td>
<td>13</td>
<td>1</td>
<td>+</td>
</tr>
<tr>
<td>Castle Bromwich</td>
<td>17</td>
<td>Nothing</td>
<td>1,200</td>
</tr>
<tr>
<td>Water Orton</td>
<td>20</td>
<td>Nothing</td>
<td>375</td>
</tr>
<tr>
<td>New Swinmore</td>
<td>22</td>
<td></td>
<td>560</td>
</tr>
<tr>
<td>Lea Marion</td>
<td>25</td>
<td>14</td>
<td>69</td>
</tr>
<tr>
<td>Faverley</td>
<td>30</td>
<td>69</td>
<td>115</td>
</tr>
<tr>
<td>Hopwas</td>
<td>34</td>
<td>11</td>
<td>20</td>
</tr>
<tr>
<td>Elford</td>
<td>39</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>Chetswynd Bridge</td>
<td>432</td>
<td>2</td>
<td>30</td>
</tr>
</tbody>
</table>
This delayed purification was probably due to the suppression of the organisms concerned with repurification by toxic discharges in the upper Tame and tributaries. A more recent examination of the Tame and tributaries in the Birmingham district confirms this (Figure 25, page 233).

River Lark

The effect of the seasonal discharge of wastes from the beet sugar factory at Bury St. Edmunds on the flora and fauna of the River Lark was studied between 1926 and 1928. For 14 days after the opening of the 1926–7 season on 21 September there was no discharge. After this period the stored fermented wash waters were then discharged with disastrous results. Fish surfaced and died as far as 7 miles downstream; the invertebrates in the factory leet and at Fornham, 1 mile below, were almost completely wiped out whilst 6 miles below only leeches survived. Following this, only unfermented wash waters were discharged. 14 days after pollution began sewage fungus appeared for about 4 miles below the factory and also downstream of a sewage effluent at Lackford for half a mile. Within a month the whole river for 12 miles was filled with sewage fungus and this continued until after the discharges ceased at the end of February. It then rapidly decreased and by the middle of April had all disappeared. Before then, however, it had become colonized with diatoms.

The fauna recovered more slowly. In the factory leet with improvement in oxygen conditions the increased food supply at first supported a large population of worms but as the food was depleted and other competing animals reappeared they decreased in numbers. One mile below the factory animals characteristic of the stony bed began to reappear in April and May and by August the silt fauna which had colonized the stony reaches during the pollution, were replaced by the normal fauna. At Lackford, 6 miles below the leet, the fauna did not fully recover before the start of the next campaign. The difference was probably due to the distribution of tributary streams from which colonization occurred. During the summer there were luxuriant growths of plants with associated fauna; diatoms were succeeded by encrusted algae and fish were present.

The 1927–8 season began early in October and the discharge of unfermented wash water continued from then throughout the season. This resulted in a more gradual deterioration in conditions but the sewage fungus followed a similar pattern to the previous season.

The Bristol Avon

The effect of milk wastes on the flora and fauna of the Bristol Avon during 1935 and 1936 was studied. During the first year both
the wastes from churn and floor washings and condenser water were discharged to the river; during 1936, however, only the condenser water was discharged with the result that the pollution was decreased. Immediately below the discharge there was a reduction in the algal growths but some distance below there was a marked increase; during the second year, when the pollution was less, this algal peak was nearer the discharge. Below the effluent similar species were found to those above including *Navicula viridula* and *Surirella ovata* in the spring and *Cocconeis*, *Chamaeisiphon* and *Uliella* in the summer.

Table 44. Comparison of fauna above and below milk waste effluent in the Bristol Avon. 

<table>
<thead>
<tr>
<th>Above effluent</th>
<th>Rare or absent</th>
<th>Below effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Chironomidae</em></td>
<td><em>Asellus</em></td>
<td><em>Epeobdella ortoculata</em></td>
</tr>
<tr>
<td><em>Nemoura</em></td>
<td><em>Epeobdella ortoculata</em></td>
<td><em>Chironomidae</em></td>
</tr>
<tr>
<td><em>Polycorpus</em></td>
<td><em>Glossiphonia complanata</em></td>
<td><em>Gammarus pulex</em></td>
</tr>
<tr>
<td><em>Baris</em></td>
<td><em>G. heterocelis</em></td>
<td><em>Helobdella stagnalis</em></td>
</tr>
<tr>
<td><em>Sphaerium corneum</em></td>
<td><em>Lumbriculidae</em></td>
<td><em>Tubificidae</em></td>
</tr>
<tr>
<td><em>Pisidium amnicum</em></td>
<td><em>P. henlowianum</em></td>
<td><em>Erpobdella octoculata</em></td>
</tr>
<tr>
<td><em>Tubificidae</em></td>
<td><em>Erpobdella octoculata</em></td>
<td><em>G. complanata</em></td>
</tr>
<tr>
<td><em>Chironomidae</em></td>
<td><em>Lumbriculidae</em></td>
<td><em>G. complanata</em></td>
</tr>
</tbody>
</table>

In addition, below the effluent, *Gongrosira schmidlei*, *Stigeoclonium farctum* and *S. tenue* were present in the summer and *Nitzschia decipiens*, *N. pales* and *Rhizosolenia curvata* were more abundant. *Chydora glomerata* was present below but not to the same extent as in the Tees. A luxuriant growth of sewage fungus was observed below the effluent but during the summer it had disappeared three-quarters of a mile below. A comparison of the fauna above and below is summarized in Table 44. It will be seen that *Gammarus* was still present below although less frequent. During the first year the discharge of the effluent resulted in slight increase in the density of organisms but with the improved conditions in the second year a further marked increase took place, as shown in Table 45. The community was much the same in both years although in the second year species of *Simulium* appeared.

General
The examples of organic pollution outlined above all concern the discharge of putrescible organic matter. The effects of such di-
BIOLOGICAL ASPECTS OF RIVER POLLUTION

Charges on stream communities are complex. Firstly the increase in organic matter results in an increase in the micro-organisms which are able to utilize it as food. These organisms form the basis of certain food chains the organisms in which thereby benefit, e.g. bacteria→Protozoa→Chironomid larvae→leeches. In cases of severe pollution other micro-organisms such as algae are suppressed and the food chains of which they form the basis are thus affected, e.g. algae→may-flies→dragon-flies.


<table>
<thead>
<tr>
<th>Distance below effluent</th>
<th>300 yd.</th>
<th>0-7 miles</th>
<th>2-5 miles</th>
<th>4-8 miles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1935</td>
<td>144</td>
<td>56</td>
<td>23</td>
<td>24</td>
</tr>
<tr>
<td>1936</td>
<td>3,277</td>
<td>562</td>
<td>465</td>
<td>465</td>
</tr>
</tbody>
</table>

The increase in the amount of detritus on the stream bed resulting from pollution favours the detritus feeders such as the Tubificids, *Aellopos* and *Sphaerium* and thereby their predators such as leeches and *Sialis larva*.

Secondly, the depletion of oxygen, resulting from the increased activity of micro-organisms, further restricts the numbers of species even of those groups which could benefit by the increased food supply and in severe pollution even these species are restricted to a few individuals. Progressive improvement, however, first permits such species to flourish and in the absence of inter-specific competition they occur in prodigious numbers, e.g. the Tubificids, Chironomids and Sphaeridae (*Tables 40 and 41*). With further improvements an increasing number of species establish themselves until a balanced community is again established.

Another factor influencing the fauna in the stony stretches is the accumulation of silt in the growths of sewage fungus on stones. *Figure 20* shows the weights of total solids compared with the weights of organic matter deposited on microslides after periods of immersion in the river Lark. It is seen that in the spring period of diatom abundance the organic matter laid down was almost as great as in...
the sewage fungus period which coincided with the beet sugar campaign. The total solids deposited, however, were much greater during the sewage fungus period. Under these silted conditions the stony rapid reaches were invaded by the normal mud-dwelling forms such as *Asellus*, *Sialis* and Lamellibranchs. In the Lark these completely replaced the normal stone fauna such as *Gammarus* and may-fly nymphs. It was assumed that this was due to deoxygenation eliminating the stone fauna which normally restricted the mud dwellers to the silted zones of lower oxygen concentration. In the Bristol Avon, however, and in some Midland streams, where although the growth of sewage fungus has resulted in the silting of the stony reaches there is little deoxygenation, both *Asellus* and *Gammarus* communities are found living side by side. It would appear, then, that the absence of silt on the stones under normal conditions limits the distribution of the mud fauna and that pollution, besides reducing their competitors by deoxygenation, provides the necessary silted conditions.

Because of the different natures of organic pollutants the two factors, high organic content and low dissolved oxygen, are not always congruent. Sewage is usually highly populated with micro-organisms responsible for its breakdown and its dissolved oxygen is low; its discharge to a stream therefore results in deoxygenation which affects the macrofauna. Other organic pollutants, however, may contain few micro-organisms and have relatively high dissolved oxygen concentrations. In such cases their discharge to the stream results in little deoxygenation and the fauna is little affected by this factor, e.g. the discharge of milk wastes into the River Avon. In both cases, however, the organic content may be high and result in prolific growths of sewage fungus which is tolerant of a wide range of oxygen concentrations. It is thus possible
to find organisms, such as *Gammarus* and may-fly nymphs which are typical of well-aerated waters, living amongst tufts of sewage fungus.

The effect of combined toxic and organic pollution further complicates the picture. Streams so affected may contain a high concentration of putrescible organic matter and yet because of the presence of toxic material its decomposition is inhibited and there is little deoxygenation. Sewage fungus and the macrofauna are also restricted by the toxic substance as in the Tame near Birmingham which, as mentioned previously, runs through the Black Country and Birmingham to the River Trent.

**BIOLOGICAL DETECTION AND ASSESSMENT OF POLLUTION**

From the above outline of the effects of pollution on the flora and fauna of streams it would appear that in the detection and assessment of pollution, biological examinations, as well as physical, chemical and bacteriological tests would be used. In this country, however, biological methods have in the past been neglected by the several authorities responsible for pollution prevention work with few exceptions, e.g. the Trent River Board and the former West Riding River Board (now the Yorkshire Ouse River Board). The purpose of this section is to illustrate the use of biological indicators but unlike the other tests, no rule of thumb method of biological assessment is as yet possible, nor indeed is it likely to be. Biological communities are complex systems and cannot be reduced to exact numerical values to be entered in neat columns alongside analytical results. In some cases to follow fluctuations of a known source of pollution the usual standard physical and chemical tests may prove more practicable. Nevertheless it is only by considering the effect on the plant and animal communities that a full picture of pollution can be obtained.

Before discussing methods of biological assessment it is first necessary to discuss the use of the term pollution. Legal aspects have been dealt with in a previous chapter. Biologically, toxic pollution occurs when the discharge of a substance reduces the numbers of individuals or restricts the number of species of plants and animals which would exist in the stream under natural conditions. Organic pollution is more difficult to define as it is a degree of a naturally occurring phenomenon and can only be defined subjectively. To consider it as occurring when a discharge causes any change in the nature of the stream community would include cases of organic enrichment which by providing basic nutrient material enrich the stream life. Man may be considered as an animal, the disposal of whose waste products is a natural phenomenon but because he
has created dense centres of population he must necessarily control this process so that it does not interfere with his hygienic, utilitarian, recreational or aesthetic interests. Thus although man's activities must inevitably affect stream life, organic pollution may be considered as the discharge of putrescible organic matter to that degree which results in an adverse change in the plant and animal communities.

The method of biological assessment of pollution that takes into consideration the effect on the whole range of species within the several communities is obviously the most ideal. An approach to this is to be found in a system evolved in the U.S.A. by Dr. Ruth Patrick. This system, which measures the degree of the upset of the biodynamic balance, involves a comparison of the number of species in different groups found at the station under examination with the average numbers of those present at several healthy stations. The organisms are divided into seven groups (Table 46), the ones in each group being considered to behave similarly under the same ecological conditions. The results are expressed as histograms each having seven columns representing the seven groups (Figure 21), the height of the column representing the numbers of species present expressed as a percentage of those present at the healthy stations. When any species is represented by a large number of individuals the corresponding column is double width. In interpreting the results the relative heights of the various columns

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Figure 21. Typical histograms of various degrees of pollution. For explanation see text. Reproduced with permission from R. Patrick, Biological measure of stream conditions, (1950), by courtesy of the Federation of Sewage and Industrial Wastes Associations, Washington 16, D.C.
to each other rather than the absolute height of any one is taken as the criterion of pollution. Figure 21 shows the histograms for four stations of varying pollution. At healthy stations where a balanced population results in a great variety of species it is found that columns I and II varied greatly depending upon the ecological position. At semi-healthy stations where the balance of life was upset a given species may be represented by a large number of individuals. Also species in one column may be more frequent than normal, whilst other columns are greatly depressed. In polluted stations certain columns may be absent and others above 100 per cent.

Table 46. Taxonomic grouping of organisms and interpretation of results of Ruth Patrick’s system of biological measurement of stream condition. Reproduced with permission from R. Patrick, ‘Biological measurement of stream conditions’, by courtesy of the Federation of Sewage and Industrial Wastes Associations, Washington 15, D.C.

<table>
<thead>
<tr>
<th>Column</th>
<th>Organisms</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>The blue-green algae, Stigcodonium, Spirogyra, Tribonema, and certain rotifers</td>
</tr>
<tr>
<td>II</td>
<td>Oligochaetes, leeches and pulmonate snails</td>
</tr>
<tr>
<td>III</td>
<td>Protozoa</td>
</tr>
<tr>
<td>IV</td>
<td>Diatoms, red algae, and most green algae</td>
</tr>
<tr>
<td>V</td>
<td>All rotifers not included in I plus clams, prosobranch snails and tri-cladid worms</td>
</tr>
<tr>
<td>VI</td>
<td>All insects and crustacea</td>
</tr>
<tr>
<td>VII</td>
<td>All fish</td>
</tr>
</tbody>
</table>

Stream condition

Healthy . . . . Col. IV, VI and VII all above 50 per cent

Semi-healthy .

(a) Either or both Col. VI or VII below 50 per cent and Col. I or II under 100 per cent, or
(b) Either Col. VI or VII below 50 per cent, and Col. I, II and IV 100 per cent or over, or Col. IV is double width

Polluted .

(a) If either or both of Col. VI and VII are absent, and Col. I and II are 50 per cent or better, or
(b) If Col. VI and VII are both present, but below 50 per cent then Col. I and II must be 100 per cent or more

Very polluted .

(a) If Col. VI and VII are absent and Col. IV is below 50 per cent, or
(b) If Col. VI or VII is present, but Col. I or II is less than 50 per cent
This method approaches the ideal but the complete examination of all species requires the services of a team of specialists. Also the natural restriction of the number of species due to physical limitations, as found in some highland brooks, is not allowed for in the scheme. In practice other methods based on different groups of organisms rather than on the entire community, although they do not give so full a picture, are still valuable and more practicable where resources are limited. Different workers according to their particular interests have used different groups as indicator organisms. Kolkwitz and Marsson in 1908 and 1909 published lists of aquatic organisms classified according to the degree of pollution of which they were typical. KOLKWITZ has revised this list in a more recent publication and it has also been discussed and illustrated by LIERMANN. These authors classify degrees of organic pollution as (a) Polysaprobic, grossly polluted; (b) Mesosaprobic, which is subdivided into α-mesosaprobic, polluted, and β-mesosaprobic, mildly polluted; and (c) Oligosaprobic conditions, non-polluted. An outline of this system is given in Addendum I, page 240. (See also Table 47 and Figures 22 and 23.)

Micro-organisms

Bacteria abound in organically polluted waters and the abundance of such forms as B. coli is taken as indicative of sewage pollution, this organism being a normal inhabitant of the alimentary canal of man and animals. The use of such tests has become standard practice in water examination and will not be discussed further here. Bacterial abundance becomes evident in the filamentous types which form macroscopic growths such as those of the sewage fungus complex, of which Sphaerotilus natans is probably the commonest in this country. This occurs in running waters polluted by organic matter with a pH 6-0-8-0. When the organic matter is rich in protein as in domestic sewage it is rapidly broken down to ammonia and growth is thus limited. Carbohydrates, however, in water of high nitrogen content produce a luxuriant growth of Sphaerotilus and since they are more stable, the growth is more extensive as in the Lark below the effluent from a beet sugar factory. Different forms, once considered varieties, are associated with varying concentrations of organic matter or varying degrees of decomposition. PRINGHEIM has shown that different forms of Sphaerotilus, Leptothrix and Cladothrix are in fact different growth forms of one identical organism. Although Sphaerotilus occurs in both soft and hard waters, saline conditions inhibit its development. Another species, Beggiatoa alba (Plate Va) which normally inhabits waters rich in sulphur is, however, found in polluted estuaries as in the Tees. An almost pure growth of this organism was found in water receiving...
Figure 22. Animals Tolerant of Various Degrees of Pollution. P-Polytrophic, M-Mesotrophic, O-Oligotrophic.

1. Chironomus plumosus (× 3)
2. Erpetoleus tenax (× 3)
3. Limnoria mercedis (× 2)
4. Staliis bavarica (× 2)
5. Aulius aquaticus (× 2)
6. Polycelis nigra (× 2)
7. Hydrochra sp. (× 2)
8. Ancylodon fluvialis (× 2)
9. Dendrocoelum lacteum (× 2)
10. Simulium venustum larvae and pupa (× 3)
11. Glossiphonia sp. extended and contracted
12. Ephydrida sp. (× 2)
wastes from a rubber processing factory. True fungi which on the Continent are common in the sewage fungus complex are much less frequent in this country. *Leptomitus lacteus* (Plate Vb) occurs in waters where the organic matter is greatly diluted and *Fusarium aqueductum*, which produces characteristic sickle-shaped spores and often has a pink tint, is associated with acid waters. Recent preliminary work in America on the relationship between aquatic fungi and
BIOLOGICAL ASPECTS OF RIVER POLLUTION

Pollution has shown that the largest numbers of true fungi were isolated from non-polluted waters. *Saprolegnia* and *Achlya* were never found in grossly polluted waters and rarely in partially polluted ones; *Pythium* and species of *Gloeotrichia* were likewise absent. Only *Aphanomyces* showed affinity for polluted waters. (See Cooke 36.)

Another member of the 'sewage fungus' complex is *Carchesium* (Plate Vc), a ciliate protozoan. Being a bacteria feeder it is most commonly associated with sewage effluents which usually have a high bacterial content. In sewage polluted streams the luxuriant tassel growths of 'sewage fungus' are sometimes found to be almost pure cultures of this organism. The distribution of planktonic protozoa, i.e. those living freely in the stream water, in relation to pollution was studied by Lackey 37. The colonial Volvocales such as *Eudorina*, *Pandorina* and *Gonium* were characteristic of polluted waters. Of the two flagellates which were found to react sharply to pollution by declining in numbers, one, *Ochromonas*, is rare in this country and the species of the other, *Cryptomonas*, are described as favouring waters rich in organic substances. The ciliates fell into two groups; the pollutional types, generally the bacteria feeders, and the non-pollutional types whose food was more varied. Gray 38 found that the ciliate fauna of a Cambridgeshire chalk stream was determined by the bacterial flora. He considered that the ciliate fauna of stream and soil were largely identical and that peaks in abundance of ciliates in the stream after heavy rains or drought when the soil crumbled into the stream were due to inoculations of soil bacteria and ciliates. The bacteria-eating ciliates such as *Paramaecium* and *Colpoda* were associated with Gram-negative rods, which, due to crop rotation, were abundant in the soil. Thus although these ciliates indicate bacterial pollution they may be derived from soil in the absence of sewage as such. Mohr 39 found few examples of good indicator protozoa in plankton, most of the critical indicators being benthonic, i.e. associated with the stream bed or banks. The use of suspended samplers such as microslides were susceptible to variations due to such varying factors as current, etc. Although some good indicators of pollution occurred they were only frequent in a narrow band of the sewage spectrum. The different reactions to pollution of similar species of the same genus necessitates specific identification and thus limits the value of such indicators. Certain species of *Chlamydomonas* and *Vorticella*, for example, are found in polluted waters and others in clean waters. Seasonal variations in numbers of some groups also restrict their value; the Euglenida, for example, show a maximum in the summer months.

Planktonic algae in the Tees were reported to be derived from
ASPECTS OF RIVER POLLUTION

growths on the river bed \(^{25}\); it seems probable that in all such fast flowing rivers they cannot be regarded as true plankton as those in lakes, ponds and sluggish rivers. BUTCHER \(^{40}\), as a result of the examination of several rivers, found that different communities of sessile algae are typical of varying degrees of pollution. At the lower end of polysaprobic zones, the filamentous alga *Stigeoclonium tenue* (Plate VII) becomes common. The diatoms *Nitzschia palea* and *Cymbella parvula* are characteristic of the mesosaprobic zones whilst *Cocconeis placentula* (see Plate VII), *Chamaesiphon sp.* and *Ulvella frequens* are restricted to oligosaprobic conditions. In the Tees, however, *Cocconeis placentula* was reported to be present in communities found below sewage effluents \(^{25}\). Here, however, the pollution was slight and its appearance was probably due to the increase of mineral salts below the sewage effluents. The added nutrient material below effluents often causes a more abundant growth of algae in the recovery zone than above the source of pollution. *Cladophora* (Plate VII) although listed by Kolkwitz as oligosaprobic is often found in the recovery zones together with *Rhizoclonium hieroglyphicum*. In such conditions these two filamentous algae are often coated with encrusted diatoms such as *Gomphonema* and *Rhoicosphenia curvata* (Plate VI). *Vascheria sp.* occurs in \(b\)-mesosaprobic conditions and *Ulothrix sp.* in \(a\)-mesosaprobic zones but difficulties in differentiating them from other species of these genera which occur in other zones limits their value as indicators. This also applies to other algae including some desmids and the Chlorococcales, some species of which occur in polluted waters.

Macrovegetation

Flowering plants are less sensitive than the microflora and although they are not found in the most polluted zones their abundance may be increased some distance below an effluent due to added nutrient materials which become deposited on the river bed. The deposition of silt on the stony bed of a stream permits the growth of a silted type of community; this includes *Potamogeton pectinatus*, *P. interruptus*, *Ranunculus fluitans* and *Elodea canadensis*. The prolific growth of these plants may give quite a pleasing but misleading impression of a seriously polluted river.

Macrofauna

The most popular group of indicator organisms, it would seem, are the invertebrate animals of the stream bed. On the basis of his observations on the Illinois river, Richardson \(^{23}\) classified the bottom dwelling animals into ten groups according to their degree of tolerance to pollution. In this country \(^{25}\), on the Continent \(^{41}\).
and in America they have been used in river surveys. Although below the index value of the different groups is discussed separately, it is the nature of the different animal communities rather than the presence or absence of any definite species that should be considered in assessing pollution.

**Platyhelminthes**

*Polycelis nigra* and *Dendrocoelum lacteum* are to be found in β-mesosaprobic zones but other species of planarians are restricted to oligosaprobic conditions. Their distribution, however, is often local and this limits their value as indicators, their absence from samples not being significant by itself.

**Annelida**

Of the worms, *Tubifex tubifex* is probably the most tolerant. It is found in the polysaprobic zone, though in the foulest conditions even its numbers are limited. Other species representing all the different aquatic families are found in polluted waters; *Lumbricus rubellus*, a relative of the common earth worm, *Lumbricillus lineatus*, *Lumbriculus spp.*, and *Limnodrilus spp.*, are all α-mesosaprobic forms, the last also occurring together with *Tubifex* in polysaprobic conditions. *Nais* is less tolerant of pollution and is now classified as β-mesosaprobic. Of the few species of leeches which are found in British streams *Erpobdella octoculata*, *E. testacea*, *Helobdella stagnalis*, *Glossiphonia complanata*, *G. heteroclita* and *Haemopis sanguisuga* may all be found in β-mesosaprobic zones where because of the abundance of their prey such as *Asellus* and chironomid larvae they are common. Of these *Erpobdella octoculata*, *Helobdella stagnalis* and *Glossiphonia complanata* are the most tolerant and may be met with in α-mesosaprobic zones.

**Arthropoda**

In hard water streams the distribution of two common crustacea *Gammarus pulex* and *Asellus aquaticus* can be used as a useful guide to the degree of pollution. Both are scavengers, but whereas *Asellus* can withstand considerable deoxygenation *Gammarus* requires a high oxygen content. *Gammarus* in well aerated water is present in most stream habitats but with reduction in the oxygen concentration it first becomes restricted to better aerated rapids or vegetation and in cases of serious deoxygenation it is eliminated altogether. *Asellus* is normally restricted to the muddy bottoms of the slow flowing stretches, but in polluted waters it invades the vegetation and the stony rapids as previously described. Observations have shown that *Gammarus* favours the smaller streams where it is often found in large numbers. In the larger streams, however, such as the Blythe
near Birmingham, although not restricted by pollution it is much less common. A similar distribution was observed in Yorkshire streams. Aquatic larvae of insects are common and widespread in most streams and provide a useful indication of the degree of pollution. *Eristalis tenax*, the rat-tailed maggot is able to tolerate the most polluted conditions but is not always present in such zones. In slightly less polluted zones the red blood worms, larvae of the *Chironomus plumosus* group, are often abundant. Other species of Chironomids occur in varying degrees of pollution and work at present being carried out on the distribution of this group in relation to pollution should prove of great value. In the Simuliidae, another family of dipterous flies, identification of the larval and pupal forms is possible and it has been found that three species, *Simulium ornatum*, *S. reptans* and *S. aureum*, are more tolerant than the other species. Of the other insects the alder-fly larvae *Sialis lutaria* and the net spinning caddis *Hydropsyche sp.* are found in α- and β-mesoprobic zones respectively. Stone-flies and may-flies are most typical of good quality streams though some species of the latter may persist in reduced numbers in mildly polluted zones; a species of *Baetis*, probably *B. rhodani*, which is abundant in many Midland streams, have been found associated with *Gammarus and Asellus* among sewage fungus below sewage effluents. Large numbers of different species of may-fly, however, are a reliable indication of satisfactory conditions. Because of the periodic emergence of adult insects and the resultant seasonal variation in the numbers of larval forms, together with the possible migration of them from one habitat to another, the absence of any species at any one station at a given time may not be significant.

**Mollusca**

Although considered intolerant of toxic pollution the Mollusca are not as a group valuable indicators. In the Illinois river *Musculium transversum* was abundant in the polluted zones but it was also common in other zones. In this country certain species of *Lymnaea*, *Sphaerium* and *Planorbis* have a similar distribution; the limpet, *Ancylistraum fluviatile* and *Hydrobia sp.* are less tolerant.

Fish are dealt with in Chapter 7, but of the bottom fauna, the stone loach, *Nemacheilus barbatula*, is more tolerant than the Miller’s Thumb, *Cottus gobio*, which is only found in good quality streams.

It is encouraging to note that research on the distribution of organisms in relation to pollution is now being carried out by various bodies and this should provide further information for use in practice. The plankton indicators are like the bacteria counts and chemical tests, indicative of conditions prevailing at the time of sampling and may be applied when frequent samples are taken.
The nature of the flora and fauna of the stream bed, however, is more indicative of general conditions. The micro-organisms of the stream bed are more sensitive to changes than the larger animals and therefore reflect more rapidly changing conditions. The larger invertebrate indicators, because of their longer life cycles, are more useful in detecting changes taking place over longer periods and require less frequent observations.

The Birmingham Tame and Rea District Drainage Board may be quoted as an example of an authority where biological methods are applied to assess the subsequent effects of the discharge of the effluents from its several works into the River Tame and tributary streams. In order to overcome, to some extent, the variation in flora and fauna due to the nature of the stream bed and rate of flow, stations were carefully chosen where these conditions were similar. The stretches chosen were those having a stony bottom with a fairly rapid flow; these were common in the streams concerned and were readily sampled with a hand net. In routine work no attempt was made to make quantitative counts as in the time available it was considered that the rough estimation of several samples at a station is of greater value than exact counts done on a few samples. It has been shown that a large number of samples must be taken from any given station before a statistically valid mean can be obtained. The frequency of the macrofauna is assessed as abundant, frequent, occasional, rare or absent, this assessment being based on a knowledge of their frequency in other streams in the district. Growths on the stones are examined microscopically and the nature of such growths are used, together with the estimation of the macrofauna, in determining the degree of pollution.

To illustrate the effect on the distribution of macrofauna of sewage pollution, quantitative counts were made at one station above and at eleven stations below the effluent from one sewage works. The distribution of ten dominant groups of macrofauna in relation to the discharge is shown in Figure 24 where the histogram represents the numbers found at each station expressed as a percentage of the total found at the twelve stations examined. It will be seen that except for Gammarus which was adversely affected by the pollution, the peaks of the other macrofauna all occurred below the effluent. As in the case of the Tees, below the entry of the Skerne, marked changes in the fauna took place over short distances below the pollution. Immediately below the effluent, larvae of the Chironomus plumosus group were dominant. 500 yd. downstream, however, these had almost disappeared and Asellus aquaticus was most abundant. Coinciding with the peak of Asellus aquaticus was that of its predatory leech Helobdella stagnalis. Erpobdella which feeds on Tubificids and Chironomids, and Glossiphonia, which feeds on...
other organisms such as Mollusca, showed a more scattered distribution. Tubificid worms, which are more common in the mud than in stony stretches, showed a preference for the zone below the effluent and the larvae and pupae of *Simulium* spp., mostly *S. ornatum* and *S. aureum*, were most common a short distance below. Other species of chironomids also appeared in the recovery zone but showed no sharp peak due probably to there being several different species present. Larvae of *Hydropsyche* sp. were most abundant at a distance of about one mile below the discharge.

Figure 25 represents in a diagrammatic form the biological conditions of some of the streams in the Birmingham district as assessed during the years 1948–53 using the methods described above. Results of standard chemical tests for the most part agreed with the biological findings but with some interesting exceptions. The

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Figure 24. Percentage distribution of some animals in relation to organic pollution
Langley Brook (1953)
Figure 25. Biological indication of pollution of streams in the Birmingham area.
River Tame between Newton Green and Perry Barr was typically polysaprobic and this was in agreement with the low dissolved oxygen, high ammonia and organic nitrogen, high 5-day B.O.D. and high 4 hours permanganate oxygen absorption. At the next station, however, Salford Bridge, all forms of macrofauna were absent or very rare, and these conditions persisted until below Curdworth. This was probably due to a large volume of toxic metallic discharges, and confirms the previous observations by Butcher. The analytical results, however, do not indicate any deterioration in conditions. The marked rise in dissolved oxygen, due to the suppression of biological activity by the toxic materials, would in themselves suggest improved conditions. Below Coleshill, probably due to the diluting effect of large volumes of sewage effluent from the Minworth and Coleshill works and from the rivers Blythe and Bourne, there is a recovery in the fauna and biological activity is again re-established as reflected by the progressive decrease in dissolved oxygen down as far as Tamworth. A similar effect was observed in the River Cole at Warwick Road where there was a marked decrease in the numbers of species and individuals. Again this deterioration was not suggested in the routine chemical results and as before the dissolved oxygen was high; toxic pollution was again the probable cause. A further case concerned the effluent from a small land treatment works which discharged to a small tributary stream of the Blythe. Biological examination of the stream indicated considerable pollution but systematic chemical tests indicated an effluent of good quality. More frequent chance sampling, however, showed that although at most times the effluent was in fact very good, occasionally, due to certain works practice in tank emptying, crude sewage was being discharged to the stream which accounted for its biological condition.

The method outlined above, although far from involving complete examination of the stream life, has proved of value in supplementing the chemical tests.

**PATHOGENIC ORGANISMS AND POLLUTION**

Apart from the saprophytic bacteria such as *Pseudomonas* and *Proteus* which play their role in the breakdown of organic matter, other bacteria of human or animal origin are also discharged in sewage effluents. One of these, *Bacterium coli*, is a normal inhabitant of the human intestine and its presence in waters is taken as indicative of contamination with human excreta. These organisms are capable of fermenting lactose broth with the production of gas and this is made use of in the presumptive coliform test for polluted waters. The numbers of bacteria as measured by the numbers of colonies
developing on nutrient agar plates after three days incubation at 22° C is taken as a measure of the degree of organic pollution. The numbers developing after incubating for 48 hours at 37° C is taken as a measure of the bacteria derived from faeces, as these develop best at body temperature (37° C) at which temperature the growth of the majority of other bacteria is checked. Other intestinal bacteria have been found to be generally associated with sewage effluents and are used as indices of pollution; these include the Streptococci and Clostridium welchii. The latter, however, are not present in large numbers and may be derived from sources other than sewage; their resistant spores may persist for long periods in polluted waters and their presence does not therefore necessarily indicate recent contamination. For the same reason, however, its presence may serve as an indication of intermittent pollution after other indications such as B. Coli have disappeared. It is considered that in the examination of mud samples B. Coli and Str. fecalri counts together probably constitute the best index of faecal pollution. These organisms, however, are largely confined to the surface layers of mud.

B. Coli is not itself pathogenic but its presence indicates faecal pollution and the possible contamination of the water with pathogenic bacteria. Although today cholera is unknown in Britain, less than a century ago it was responsible for many deaths and was spread by contamination of water supplies. During an epidemic in Hamburg in 1892, Dunbar isolated the responsible organisms, Vibrio cholerae, from the polluted Elbe. Typhoid fevers although uncommon today were also prevalent a century ago and these also are water-borne diseases, the responsible organisms Salmonella typhi, previously called Bacterium typhosa, and S. paratyphi having been isolated from sewage effluents and receiving streams during times of epidemic. It was calculated that during the paratyphoid B. epidemic at Epping in 1931, 143 billion paratyphoid B. organisms were discharged on one day to a tributary stream of the River Lee which is one source of London’s water supply. Two further groups of the bacteriaceae, other Salmonella which causes food poisoning and Shigella, one organism responsible for dysentery, have frequently been isolated from polluted streams. A recent outbreak of gastro-enteritis in a factory was found to be due to the contamination of the factory drinking-water by polluted river water from which Shigella sonnei was later isolated. Several Salmonella organisms have been shown to be common to man and other animals and it therefore appears that pollution of streams by animals may provide a source of contamination.

Although S. typhi, S. paratyphi, other Salmonella and Shigella are the most common pathogenic bacteria in polluted waters in
Britain, other pathogens such as \textit{B. anthracis} have been isolated from sewage effluents and polluted streams. It is not always possible to trace outbreaks to specific sources and in many cases the presence of pathogens in stream water although indicating a potential danger does not in itself prove that the disease is spread by the polluted streams. The virus responsible for poliomyelitis has been isolated from polluted streams and it would seem that such water could be a source of infection for cattle which drank it. However, cows drinking stream water containing the organism as a result of pollution from a slaughter house, were not infected; nor were cattle drinking water from a stream receiving dairy waste waters. The discharge of sewage effluents into streams which are used as drinking-water for cattle is generally viewed with mistrust by farmers. It is stated that cattle often prefer sewage effluents to fresh water even when drinking troughs are provided. Brucellosis, which in cattle gives rise to a feverish condition and contagious abortion, mastitis and tuberculosis have all been suspected of being transmitted in such a manner. It seems probable, however, that these are as likely to result from contamination of water upstream by infected cattle as from sewage effluents.

In this country few detailed bacterial studies on rivers have been undertaken. In the Avon it has been shown that the plate counts on nutrient agar at 20°C and 37°C, the presumptive counts of coliform bacteria at 37°C and 44°C and the presumptive counts of faecal streptococci all increased greatly below sewage effluents. With increasing distances below the discharge, however, the counts rapidly decreased, this being most marked with the coliform bacteria and faecal streptococci. Below one effluent, for example, the count of faecal streptococci decreased by 97 per cent in less than 3 miles and in another case by almost the same amount in 1.9 miles. This rapid decrease was not accounted for by dilution. Several factors were probably involved; these include natural death in absence of nutrient material, settlement possibly preceeded by flocculation, together with the solid matter to which they become attached, predatory activity of protozoa and other bacteria feeders, the presence of bactericidal substances and bacteriophage. The bacteriophage for \textit{Clostridium welchii} and the typhoid Vi bacteriophage have been isolated from polluted waters in quantities proportional to the degree of pollution. It has been suggested that the presence of Vi bacteriophage in water might be used as an indication of recent pollution by typhoid organisms. The degree of anaerobiosis may also affect the viability of faecal organisms; it was
found that under anaerobic conditions *B. coli* died more rapidly than under aerobic conditions. *Str. faecalis*, however, were not affected by the degree of oxygenation.

In Britain, water-borne diseases of man are nearly all bacterial in origin but elsewhere higher organisms in contaminated waters may attack both man and cattle. The protozoan *Entamoeba histolytica*, which causes a form of dysentery in humans, is spread by contaminated waters. The eggs and young stages of several parasitic worms find their way in sewage effluents into streams where after further stages in development they are liable to infect users of the water. In Africa a parasitic Trematode worm *Schistosoma* (*Bilharzia*) lives as an adult in the abdominal veins of man. The eggs pass via the blood vessels to the bladder and are then discharged in the urine. On entering water they hatch into a larval form and before further development takes place these must enter the second host, a water snail, *Oncomelania*. As the larvae die within 24 hours if they do not succeed in finding the snail, efficient sewage treatment probably kills them whereas the discharge of untreated sewage or urine to streams favours their development. Detection of pollution by *B. coli* counts, although a measure of faecal pollution, does not indicate contamination by urine alone in which the worm is discharged. Certain other flukes which attack cattle have a similar life cycle involving free living aquatic stages and are thus spread by contaminated streams.

Eggs of Tapeworms (Cestoda) and parasitic Nematode worms are common in crude sewage and the discharge of untreated sewage to streams results in contamination of the water with resultant danger to man and beast. After World War II there was a widespread infection of *Ascaris* at Darmstadt in Germany and during a subsequent investigation crude sewage was found to contain 5,400 *Ascaris* eggs per litre. Other work showed that *Enterobius*, another parasitic Nematode, were more common than *Ascaris*; in Berlin sewage, eggs of *Tania* were also present. In sewage treatment, efficient sedimentation removes most of the eggs with the sludge but these remain viable for long periods in air-dried sludge and form a source of infection when the sludge is used as a fertilizer. At Stuttgart it was found that 80 per cent of the worm eggs were removed by sedimentation and that digestion of the sludge killed all the eggs. In South Africa, however, it was found that 45 per cent of the *Ascaris* eggs in digested sludge were viable and although after four months drying no viable eggs were found in the upper layer, they were present at a depth of 3 in. As a result of observations on the effect of various processes of sewage treatment on the destruction or removal of eggs of *Tania* from sewage, it was concluded that under normal operating conditions an appreciable
number of eggs would escape in the primary tank effluent. Filtra-
tion through percolating filters removed 62-70 per cent and pro-
longed activated sludge treatment had little effect. After digestion
at 75-78 °F for over 200 days 10-15 per cent of the eggs remained
viable. It was concluded that sand filtration was the most efficient
method of removal. At Coventry, however, rapid sand filtration
has proved ineffective in retaining eggs of both Tania and Ascaris.
Besides the direct discharge of viable pathogenic organisms into
streams, pollution may also bring about a change in the animal
population which favours the life cycle of these pathogens. In
Natal, observations have shown that pollution has shifted the bal-
ance of population in favour of the mollusca which act as hosts of
the Schistosomes. In New Jersey mosquito breeding has been
found to be favoured by pollution. The association of certain
species of Simulium with pollution may prove to be a factor in the
prevalence of several diseases of which these flies are the vectors.
Considering the potential danger of the discharge of pathogenic
organisms in sewage effluents and storm water discharges and the
use of river water as sources of domestic supply, surprisingly little
attention is paid in this country to their bacterial content. In the
U.S.A. bacteriological examination of effluents is common practice
and sterilization of them by such processes as chlorination is widely
practised. Such treatment, however, although reducing the bac-
terial content, must necessarily affect the stream life. In this
country it is the policy to maintain our streams as living com-
munities and effect purification of water for domestic use after
withdrawing. At the same time it is in the interests of public health
to reduce to a minimum the number of pathogens in effluents by
efficient sewage purification followed where necessary by sand
filtration or micro-strainers.
The efficiency of different methods of sewage purification is
usually assessed by chemical standards and little attention is paid
to the removal of intestinal bacteria. The chemical quality of an
effluent, however, is no guide to the number of faecal bacteria
it may contain. In a single percolating filter although an appreci-
able reduction in the B.O.D. of the sewage took place in the upper
layers, large reduction in the numbers of bacteria only occurred
in the lower levels. At a rate of treatment of 60 gal./yd.3/day
single percolating filtration removed more than 90 per cent of the
bacteria during the warmer months, but in the winter the percentage
removed fluctuated considerably and was sometimes quite low.
Alternating double filtration, although producing a chemically
satisfactory effluent at higher rates (about 240 gal./yd.3/day),
edected a much smaller removal of bacteria. Although sand filtra-
tion further reduced the numbers of bacteria it was considered that
this treatment could not be relied upon to produce consistently an effluent of good bacterial quality. Different methods of treatment may result in a differential removal of the various intestinal bacteria. Comparison between large-scale sewage works and small domestic sewage plants, involving septic tank treatment, showed that in the latter Str. faecalis was removed far more effectively than was B. coli.
ADDENDUM I

An outline of the revised Kolkwitz and Marsson’s ecological system of saprobes

The availability of food and oxygen and the chemical nature of the water are among the important factors determining the different communities in stream life. The discharge of decomposable complex organic matter such as sewage to a stream changes the nature of the plant and animal communities to an extent depending upon the degree of pollution. As self purification proceeds different communities become successively established. KOLKWITZ and MARSSON 61, 62 distinguished three zones of existence; recently the system has been revised 31, 32 in light of later work (see Table 47).

1. POLYSAPROBIC (P)

Characterized chemically by a high concentration of complex, decomposable organic matter (albumens, polypeptides and carbohydrates) derived from sewage discharges and some industrial effluents. Reduction and splitting processes bring about decomposition, oxygen being absent or present in traces only. H₂S is produced, so considerable odour is present. Black sludge deposits containing sulphides accumulate on the bottom.

Characterized biologically by the restriction of the community to a few groups, the individuals of which may, however, be present in prodigious numbers; bacteria and protozoa being the most common groups. Culture counts of >10⁶ per ml. can be obtained. If pollution is due to sewage, B. coli are abundant but not if due to cellulose, dairy or brewery wastes.

2. MESOSAPROBIC (M)

Chemically defined by well-established oxidation processes both in the water and sludge. Subdivided into two zones:

a-Mesosaprobic (α-M) zone contains a high content of amino-acids arising from the breakdown of complex compounds. The oxygen content may be considerable and because of the development of chlorophyll-containing organisms, especially algae, the oxygen content increases by day and declines by night. As a rule the oxygen content is <50 per cent of saturation. Owing to the oxidation of the black FeS to yellow brown hydrated Fe₂O₃, the bottom muds are no longer black in colour. H₂S is oxidized by the available oxygen and odour nuisance no longer exists.

Biologically, it still contains high numbers of bacteria; culture counts normally being <100,000 per ml.

b-Mesosaprobic (β-M) zone is chemically distinguished by the continuing oxidation or mineralisation and is the region of ammoniacal compounds of the fatty acids. The oxygen content is fairly high being never less than 50 per cent of saturation.
Biologically characterized by a fall in the bacteria counts to always <100,000 per ml.

In the α-mesosaprobic zone, although protozoa and the more tolerant species abound, the macrofauna, with the exception of worms, are still restricted in species. In the β-mesosaprobic zones, however, there is a great diversity of plants and animals.

3. Oligosaprobic (0)

This is the zone of completed oxidation or mineralization. Organic substances have broken down and all vigorous disintegration processes have died away. The sludge is almost completely oxidized, although here and there mesosaprobic conditions may persist. The water is clear and rich in oxygen, except on occasions when water-blooms (luxuriant growths of unicellular algae) develop and cause turbidity and, in darkness, a fall in dissolved oxygen.

Biologically characterized by a further fall in bacterial counts to <100 per ml and a wide range of species of plants and animals, including fish, is to be found.

Remarks

All animals do not fall neatly into this grouping, and some are to be found in more than one zone. Other species react more sharply to pollution and are thus more useful as indicators. Some organisms are not found in any of the saprobic zones but are only met with in springs and pure mountain streams. Such communities are termed Kalerobic.

In using this system it must be borne in mind that factors other than pollution affect the nature of stream communities. The absence of organisms may be a more important indication than the presence of other species. The community of organisms should be taken into consideration rather than the presence or absence of one or few 'indicator organisms'. The following table, based on this classification, lists some of the commoner stream organisms according to their degree of tolerance to organic pollution. In some cases specific identification is essential, in others the genera or the whole family may be indicative. Knowledge of stream ecology is continually advancing and no doubt the list will be modified and extended in light of this knowledge.
### ASPECTS OF RIVER POLLUTION

Table 47. Tolerance of organisms to organic pollution (based on Kolkwitz and Marron's classification)

<table>
<thead>
<tr>
<th>Systematic group</th>
<th>Polyasaprobie (grossly polluted)</th>
<th>α-Mesosaprobie (polluted)</th>
<th>β-Mesosaprobie (mildly polluted)</th>
<th>Oligosaprobie (non-polluted)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BACTERIA</strong></td>
<td>Mostly Spirillum zoochae ramigena</td>
<td>P and M</td>
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<td></td>
<td>Sphaerotilus</td>
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<td><strong>Fungi</strong></td>
<td>Fusarium</td>
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<td>Leptomit us lacteus</td>
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<td></td>
<td>Geotrichum sepulcriculum</td>
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<td><strong>ALGAE</strong></td>
<td>Oscillatoria spp.</td>
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<td>Chamaesiphon</td>
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<td>Cyanophyceae</td>
<td>Spirulina</td>
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<tr>
<td>(blue-green algae)</td>
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<tr>
<td>Bacillariaceae</td>
<td>Nitzschia palea</td>
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<td>(diatoms)</td>
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<tr>
<td>Chlorophyceae</td>
<td>Chlamydomonas spp.</td>
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<td>(green algae)</td>
<td>Stigeoclonium</td>
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<td>Ulothrix</td>
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<td>Oedogonium</td>
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<td>Chaetophora</td>
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<td>Vaucheria</td>
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<td>Spirogyra</td>
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<td>Cliffordia</td>
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<td></td>
<td>Cladophora spp.</td>
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<td></td>
<td>Scenedesmus</td>
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<td>Sargassum</td>
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<tr>
<td>Rhodophyceae</td>
<td>Batrachospermum and all other</td>
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<td>(red algae)</td>
<td>fresh water spp.</td>
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<tr>
<td>Bryophyta</td>
<td>Elodea canadensis (Canadian</td>
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<td>Liverworts and</td>
<td>water weed or water thyme)</td>
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<tr>
<td>mosses</td>
<td>Glyceria aqualica</td>
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<td>Angiospermi</td>
<td>Eichornia</td>
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<td>Polygynum amphium</td>
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<tr>
<td>Systematic group</td>
<td>Polytophagor (polluted)</td>
<td>ω-Mesoprophagor (polluted)</td>
<td>β-Mesoprophagor (mildly polluted)</td>
<td>Oligoprophagor (non-polluted)</td>
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<tr>
<td>ANTHOPODA</td>
<td>Potamogeton pectinatus</td>
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<td>P. intertortus</td>
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<td>Rhamnusus fluviatus</td>
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<td>Lemna minor</td>
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<td>Potamogeton</td>
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<td></td>
<td>P. rotundifolius</td>
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<td></td>
<td>Potamogeton</td>
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<td></td>
<td>P. obtusifolius</td>
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<td></td>
<td>Nuphar luteum</td>
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<td>Nymphaea alba</td>
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<td>Protozoa</td>
<td>Amoeba spp.</td>
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<td></td>
<td>Arcella spp.</td>
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<td></td>
<td>Doliugia spp.</td>
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<td></td>
<td>Euglena viridis</td>
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<td></td>
<td>Bodo spp.</td>
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<td></td>
<td>Anthophytae</td>
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<td></td>
<td>vegetans</td>
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<td>CILIOPHORA</td>
<td>Paramecium caudatum</td>
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<td>Colpidium colpoda</td>
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<td></td>
<td>Amphileptus spp.</td>
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<td>Oxytricha spp.</td>
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<td>Loinius spp.</td>
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<td>Stylosychia spp.</td>
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<td></td>
<td>Aspidota spp.</td>
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<td></td>
<td>Euolotes spp.</td>
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<td></td>
<td>Vorticella microstoma</td>
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<td>V. convallaria</td>
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<td>V. campanula</td>
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<tr>
<td></td>
<td>Carpehrium spp.</td>
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<td></td>
<td>Epistylis spp.</td>
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<tr>
<td></td>
<td>Opercularia spp.</td>
<td></td>
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<tr>
<td></td>
<td>Podophraya</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Acinetra</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>PLATYHELMINTHES</td>
<td>Dendrodium lacteum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Turbellaria</td>
<td>Planaria alpina</td>
<td></td>
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<tr>
<td></td>
<td>P. genorophala</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Polyecelis nigra</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>ANNELEDA</td>
<td>Lumbrixus rubellius</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(true worms)</td>
<td>Limnoidrillus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lumbriulus spp.</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Lumbriillus lineatus</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Styliaria</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Nais</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>Chaetogaster</td>
<td></td>
<td></td>
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</tr>
<tr>
<td></td>
<td>Gordius</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### Table 47—cont.

<table>
<thead>
<tr>
<th>Systematic group</th>
<th>Polygrophic (grossly polluted)</th>
<th>α-Mesogrophic (polluted)</th>
<th>β-Mesogrophic (mildly polluted)</th>
<th>Oligogrophic (non-polluted)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hirudinea</td>
<td>Erpobdella octoculata</td>
<td>Glossiphonia complanata</td>
<td>Helobdella stagnalis</td>
<td>Haemopis sanguinosa</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Episcobdella testacea</td>
<td>Babylonia longistriata</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anthropoda Crustracea</td>
<td></td>
<td>Daphnia spp.</td>
<td>Cypria spp.</td>
<td>Astacus fluviatilis</td>
</tr>
<tr>
<td></td>
<td>Aeolus aquaticus</td>
<td></td>
<td>Cyclops spp.</td>
<td>(freshwater crayfish)</td>
</tr>
<tr>
<td></td>
<td>(water louse)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insecta</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Plecoptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Stone-flies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ephemeroptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(May-flies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Neuroptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Alder-flies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Trichoptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(Caddis-flies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diptera</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(True-flies)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Eristalis tenax</td>
<td></td>
<td>Chironomus plumosus</td>
<td>Chironomus spp.</td>
</tr>
<tr>
<td></td>
<td>(rust-sailed maggot)</td>
<td></td>
<td></td>
<td>Taenypus spp.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Culex spp.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulium ornatum</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulium reptans</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Simulium aternum</td>
</tr>
<tr>
<td>Mollusca</td>
<td>Sphaerium corneum</td>
<td></td>
<td>Piastidium spp.</td>
<td>Unio Planoaria</td>
</tr>
<tr>
<td></td>
<td>Lymnaea auricularis</td>
<td></td>
<td>Anceus fluvitilis</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>
### Table 47—cont.

**Saprobic classification of members**

<table>
<thead>
<tr>
<th>Systematic group</th>
<th>Polyathropic (greatly polluted)</th>
<th>α-Mesosaprobic (mildly polluted)</th>
<th>Oligosaprobic (non-polluted)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pisces (Fish)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alburnus alburnus (Bream)</td>
<td>Other species e.g. Salmo fario (river trout)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anguilla anguilla (eel)</td>
<td>Esox lucius (pike)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gasterosteus aculeatus (3-spined stickleback)</td>
<td>Cottus gobio (Miller's Thumb)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carassius carassius (Crucian carp)</td>
<td>Gobio gobio (gudgeon)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carassius auratus (goldfish)</td>
<td>Perca flavescens (perch)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nemacheilus barbatus (stol cach)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
ADDENDUM II

Pathogenic organisms in sewage and polluted streams

The discharge of pathogenic organisms in the faeces and urine of infected persons results in a large number of these organisms reaching the sewage works. Some of these in normal sewage works operation are discharged in the effluent, others settle out with the sludge and become a potential danger when the latter is used as a fertilizer. In Table 48 many of the commoner water-borne diseases are listed, some are uncommon in this country today but are important in warmer countries.

Effect of sewage purification on pathogens

References to literature on the subject leave one rather confused and therefore generalization is difficult. (A good summary is to be found in Reference 63.)

(i) Although many pathogens can survive sewage treatment no evidence that they can multiply in the plant.
(ii) Danger presented by pathogens in effluents proportional to numbers present in the original sewage, i.e. real danger at times of epidemic.
(iii) Reduction in numbers of pathogenic organisms of various types—of same order as the reduction of all types of bacteria.
(iv) Although percentage reduction may be high, at times of epidemic so great is the number of organisms reaching the work that the effluent will still be dangerous.
(v) The chemical quality of an effluent is no guide as to the number of faecal organisms it may contain.
(vi) Recently reported that even sand filtration could not be relied upon to produce an effluent of good bacteriological quality. Even the eggs of Taenia (Tape worm) were found in effluents from sand filters.
(vii) Chlorination of effluents necessary to ensure absence of viable pathogens. Not practised by sewage works in this country; danger of toxic pollution to stream life.
(viii) Many organisms concentrated in sludge and although many killed in the processing some withstand digestion and sludge drying on beds.
(ix) The percentage removal of bacteria fluctuates greatly seasonally and from works to works. The following are round average figures:

<table>
<thead>
<tr>
<th>Stage</th>
<th>No. per ml.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw sewage</td>
<td>10 million or more</td>
</tr>
<tr>
<td>Settled sewage</td>
<td>2.5 &quot;&quot;</td>
</tr>
<tr>
<td>Bacteria bed humus tank</td>
<td>0.5 &quot;&quot;</td>
</tr>
<tr>
<td>effluent up to</td>
<td>100,000 or more</td>
</tr>
<tr>
<td>Sand filter effluent</td>
<td>10,000 &quot;&quot;</td>
</tr>
<tr>
<td>Land filtered effluent</td>
<td>10,000 &quot;&quot;</td>
</tr>
</tbody>
</table>
Recent advances in treatment, although producing chemically good quality effluents at higher rates, effect a much smaller removal of bacteria.

<table>
<thead>
<tr>
<th>Organism</th>
<th>Disease</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Virus</strong></td>
<td>Poliomyelitis</td>
<td>Exact mode of transmission not yet known. Found in effluents from biological sewage purification plants</td>
</tr>
<tr>
<td><strong>Vibrio cholera</strong></td>
<td>Cholera</td>
<td>Transmitted by sewage and polluted waters</td>
</tr>
<tr>
<td><strong>Salmonella typhi</strong></td>
<td>Typhoid fever</td>
<td>Common in sewage and effluents in times of epidemics</td>
</tr>
<tr>
<td><strong>Salmonella paratyphi</strong></td>
<td>Paratyphoid fever</td>
<td>Common in sewage and effluents in times of epidemics</td>
</tr>
<tr>
<td><strong>Salmonella spp.</strong></td>
<td>Food poisoning</td>
<td></td>
</tr>
<tr>
<td><strong>Shigella</strong></td>
<td>Bacillary dysentery</td>
<td>Polluted waters main source of infection</td>
</tr>
<tr>
<td><strong>B. anthracis</strong></td>
<td>Anthrax</td>
<td>Found in sewage. Spores resistant to treatment</td>
</tr>
<tr>
<td><strong>Brucella</strong></td>
<td>Brucellosis - Malta fever in man, Contagious abortion in sheep, goats and cattle</td>
<td>Normally transmitted by infected milk or by contact. Sewage also suspected</td>
</tr>
<tr>
<td><strong>Mycobacterium tuberculosis</strong></td>
<td>Tuberculosis</td>
<td>Isolated from sewage and polluted streams. Possible mode of transmission. Care with sewage and sludge from sanatoria</td>
</tr>
<tr>
<td><strong>Leptospira interrogans</strong></td>
<td>Leptospirosis (Weil's Disease)</td>
<td>Carried by sewer rats</td>
</tr>
<tr>
<td><strong>Entamoeba histolytica</strong></td>
<td>Dysentery</td>
<td>Spread by contaminated waters and sludge used as fertilizer. Common in warmer countries</td>
</tr>
<tr>
<td><strong>Schistosoma</strong></td>
<td>Bilharzia</td>
<td>Probably killed by efficient sewage purification</td>
</tr>
<tr>
<td><strong>Taenia spp.</strong></td>
<td>Tapeworms</td>
<td>Eggs very resistant, present in sewage sludge and sewage effluents. Danger to cattle on sewage-irrigated land or land manured with sludge</td>
</tr>
<tr>
<td><strong>Acaris Enterobius</strong></td>
<td>Nematode worms</td>
<td>Danger to man from sewage effluents and dried sludge used as fertilizer</td>
</tr>
</tbody>
</table>
Possible modes of transmission of water-borne disease

(i) Sewage contaminating water supplies—storm water discharges, etc.
(ii) Effluents contaminating water supplies.
(iii) Handling of sewage and sludge on works.
(iv) Grazing of cattle on sewage farms.
(v) Grazing of cattle on land fertilized with sludge.
(vi) Eating of salad vegetables from land fertilized with sludge.
(vii) Water-cress grown in effluents.
(viii) By birds and flies from bacteria beds, etc.
(ix) Fish in sewage effluents.
(x) Contamination of bathing waters.
(xi) By air-borne droplets from sewage.

Against the potential dangers of using sewage effluents and sludge must be weighed the loss of valuable fertilizers they contain; this is especially true in countries (such as South Africa) where they are in great demand.

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INTRODUCTORY REMARKS

River surveys are carried out for a number of reasons. The surveys may be merely of a routine character conducted to obtain an idea of the quality of the stream water at various points and under varying weather conditions, and if possible to assess the effect of the many pollutions. In this way, valuable data can be obtained providing a basis for a comparison of the state of the stream at different seasons and in different years. Surveys may also be undertaken for research purposes, or with the intention of formulating by-laws or taking legal proceedings under the Rivers (Prevention of Pollution) Act, 1951, or with the object of investigating some complaint such as mortality amongst fish, odour nuisance, or unsuitability of the river water for industrial and other uses. Whatever the purpose in view, the detection and identification of the particular pollution or pollutions followed by the application of quantitative methods to determine the extent of the pollution must constitute a fundamental feature of the survey. For this purpose, various procedures are available making use of hydrological, physical, chemical, bacteriological and biological techniques.* The main object of this chapter is a discussion of these various methods, but for practical details the reader is referred to the various official and other publications on the subject (see references at end of chapter, especially references 1–21).

It is rarely necessary to undertake an elaborate survey using all the methods and techniques reviewed here, and often a simple field survey utilizing a limited number of tests and methods suffices. The choice and number of methods used will depend to a large extent upon the purposes in view, on the nature of the problems encountered, on the staff and funds available, on the periods of

* Strictly speaking, bacteriological methods should be included under the heading of biological methods but it is convenient to consider them separately.
time over which observations are taken, and on local circumstances.

The sampling for a physical and chemical examination of discharges of sewage effluents and trade effluents and of stream waters forms an important feature of a river survey (see references 22–30). Samples should be taken in clean, colourless glass bottles provided with ground-in glass stoppers; half-winchester bottles holding one quart (or about 1 L) are convenient for this purpose but the amount of sample required may be more or less than this quantity depending upon the nature and composition of the sample and upon the completeness of the analysis. Certain determinations (e.g. dissolved oxygen, oil, sulphide) must be performed on a separate sample taken specially for the purpose in another bottle. It is a wise precaution when sampling to rinse the bottle once or twice with the sample. Care should be taken to see that a representative sample containing the true proportion of suspended matter to liquid is obtained and it is obvious that any deposit on the bottom of the stream, sewage fungus growing on the bed, etc., should not normally be included (such extraneous matter should be separately collected and examined).

The taking of a sample in a bottle of absolutely clear and colourless glass facilitates a general description of the appearance of the sample. The description of the settled sample should include the smell, the colour, and the degree of turbidity of the supernatant liquid as well as the colour, apparent quantity and general characteristics of the sediment (e.g. whether finely divided, flocculent, sandy, etc.). The sediment, which may include dead and living material, frequently has a characteristic appearance under the microscope, consequently a microscopic examination should rarely be omitted. Dead material may be chiefly of mineral origin (e.g. sand granules from the river bed or from a sand washery) or it may be predominantly organic (e.g. coal-dust, cotton fibres, wool, paper pulp, starch granules). Living material can include algae, filamentous organisms (e.g. 'sewage fungus'), yeast cells (from brewery wastes), protozoa, crustacea, etc., and the identification of these by biological methods frequently yields valuable information. Sewage sludges, if present, may contain dead as well as living material.

The observations of Webber are of particular relevance in connection with sampling:

'The actual collection of the water sample is a matter of considerable importance, more especially as this is often done by laymen with little knowledge of such matters. There can be few responsible chemists who have not received a grubby bottle filled with dirty water late on a Friday afternoon, accompanied by a
The label on the sample bottle should include such information as the type of sample (e.g. stream water, sewage effluent, trade effluent, etc.), the source (e.g. name of stream, firm, or local authority), the exact position of the sampling point (an Ordnance map reference may be necessary), the date, the time, the temperature of the sample, the weather and particulars of recent weather conditions, the visible state of the river (e.g. whether above or below normal flow, whether in spate), the state of the tide if the river is tidal, whether taken in the middle, left, or right bank and at what depth, and any other relevant data which might assist the analyst. The signature of the person taking the sample should also appear on the label and if possible the name of the person in whose presence the sample is taken, and the label should bear a reference number.

If a bacteriological analysis is required, a special sample should be taken under aseptic conditions in sterilized glass bottles (capacity about 200-250 ml) provided with ground-in dust-proof stoppers; if a river water is being sampled, the stopper is removed below the stream surface and against the flow. Precautions to be observed and other recommendations in connection with sampling for bacteriological tests are given in a Ministry of Health report.

River samples are often taken at a point halfway between the surface and the bed of the stream, carefully avoiding the disturbance of sediment at the bottom. Since, however, the mean velocity of a stream on any vertical is usually found at approximately 0·6 h from the surface (where h = depth) it has been suggested that sampling should be done at that depth. Much depends upon local circumstances and it may be necessary in some cases (especially near effluent outfalls) to take samples at different depths. For a fuller discussion of the precautions to be taken when sampling and of the most suitable sampling positions, the reader is referred to the literature (see especially references 1, 2, 3, 6, 7, 12 and 23).

When it is necessary to take samples at frequent intervals during the day, the use of automatic sampling devices is often desirable. Samples should be kept in a refrigerator at about 4°C if the analysis cannot be carried out immediately, since it has been shown in the case of sewage and sewage effluents that considerable changes in composition may take place on storage at ordinary temperatures owing to biochemical action.

Section 15 of the River Boards Act, 1948, specifies that where it is desired to use an analysis of a sample as evidence in legal proceedings, the occupier of the land or the local authority must be notified.
of the fact that an analysis is to be carried out. The person taking
the sample must divide the sample into three parts each of which
must be placed in a sealed bottle or container. One part is handed
to the occupier of the land or the local authority, another part is
kept for court inspection, and the third part is analysed.

When a river board wishes to make an application to the Minister
under the Rivers (Prevention of Pollution) Act, 1951, for consent
to take proceedings in respect of pollution of a stream by sewage
effluent or trade effluent the stream water should be sampled,
according to a Ministry circular, both above and below the alleged
source of pollution, and, if at all possible, a sample of the effluent
itself should be taken. It may not be amiss to add a few words on the question of the accuracy of the methods used in the chemical examination of
samples. The degree of accuracy normally attainable in chemical
work of this kind is of the order \( \pm 5 \) per cent and this is sufficient for
most routine work. For research work, a higher degree of accuracy
is desirable and for this purpose lengthy procedures are often neces-
sary involving the use of expensive apparatus and equipment and
careful attention to detail. For most routine work and field tests,
time is a most important consideration and it is desirable to use
quick straightforward methods with avoidance as far as possible of
involved time-consuming techniques using complicated apparatus.
A method having the virtues of simplicity, rapidity, and ease of
performance, in so far as these are consistent with reasonable reli-
bility, is much to be preferred to a long, involved procedure of
greater accuracy. A modern method is not always better than an
older well-tried one; indeed, the word ‘modern’ is often applied to
justify something that has little other merit. It must be remem-
bered, too, that the accuracy of a method is limited by the accuracy
of the sampling which is generally not of a very high order. The
position is well summarized by Lovett and Firth:

\[ \text{Frequently, extreme accuracy is not essential in routine testing,}
\]
\[ \text{and providing the limitations of a particular procedure are fully}
\]
\[ \text{appreciated, it may be a great advantage to make some sacrifice}
\]
\[ \text{regarding accuracy, particularly if appreciable saving in time}
\]
\[ \text{results therefrom.} \]

It is important, however, to emphasize that this does not mean that
slipshod work is condoned or that it matters little if an end-point
be overstepped by several drops of titrant. In general, then, it is
better to be prudent and use a simple straightforward method whose
errors and limitations are known rather than a so-called ‘improved’

* It may not be feasible to get a sample of the effluent if the outlet is submerged
or if the discharge takes place in a culvert.
procedure of doubtful soundness. Let us, therefore, adopt towards these newer but insufficiently tested methods a somewhat cautious attitude of mind, which, in the words of Shakespeare:

'... makes us rather bear those ills we have
Than fly to others that we know not of.'

*Hamlet*, Act III. Sc. i.

Needless to say, arithmetical calculations involved in analytical and survey work should be carefully checked either by means of a slide rule, or by the use of books of mathematical tables. Although the metric system of weights and measures is used wherever possible and chemical results are now generally expressed in parts per million (p.p.m.)*, i.e. grams per million millilitres, or milligrams per litre, large scale data are frequently determined in the imperial system and conversion from the one system to the other is often required. A few common conversion factors are given in the Appendix but a more complete list is to be found in a publication of the British Standards Institution and in handbooks of chemical and physical constants.

**HYDROLOGICAL METHODS**

Hydrological data of special significance in connection with stream pollution problems are:

(i) The measurement of the velocity of the river (in feet per second).

(ii) The determination of the river flow (in cubic feet per second, or cusecs). This is the quantity of water flowing in unit time past a particular section and is equal to the product of the mean velocity of the current and the area of the cross-section.

(iii) The estimation of the Dry Weather Flow (D.W.F.) at a sewage works (in gallons per 24 hours).

(iv) The estimation of the flow of a trade discharge (in gallons per 24 hours).

The dilution factor, or factor which expresses the proportion of stream water to sewage effluent or trade effluent is of great importance in connection with the fixing of suitable chemical standards for the discharge, and can be calculated from the ratio river flow: effluent flow. The river flow should be determined after a suitable period of dry weather as it is the minimum flow that is of importance for formulating standards for effluent discharges and for estimating the amount of water available for various industrial

* In the U.S.A., the latest edition of the A.P.H.A. *Standard Methods* recommends the use of the more precise term 'mg. per litre' instead of 'p.p.m.'
DETECTION AND MEASUREMENT

The dry weather flow of a stream (i.e. the flow determined in dry weather), however, has never been precisely defined and it is not a fixed quantity but can vary quite widely according to the particular year, to the season, and to the character of the drought period. A suggestion is, therefore, put forward in Chapter 11, (pages 410-17) for determining what it is proposed to call the 'standard flow' of the river, which is based upon a statistical evaluation of flow results over a period of at least 10 years. This is considered to be a more scientific basis for calculating dilution factors.

All flows should be expressed in terms of the same units, preferably gallons per 24 hours. River engineers generally express measurements of river flow in cubic feet but these data, to be of any value in pollution problems, must first be converted to gallons per 24 hours by the relation

\[ \text{cubic feet} \times 538,168 = \text{gallons per 24 hours}. \]

For all practical purposes, it may be taken that 1 cubic foot is equal to 538,000 gallons, and for approximate calculations it may be assumed that 1 cubic foot equals half a million gallons per day.

The determination of the velocity of a river is usually carried out by using a current meter. For the gauging of small streams, however, the use of some form of weir is necessary. A fuller discussion of these determinations is given in Chapter 11.

An approximate estimation of the velocity of a river can be obtained, according to a Ministry publication, by timing the movement of an orange over a measured stretch in the middle of the stream and assuming that the current velocity is 75 per cent of that of the speed of the orange.

Table 49, taken from the 8th Report of the Royal Commission on Sewage Disposal, shows a classification of rivers according to their current velocity, and gives the time (based on tests with fluorescein) in which mixing with sewage becomes complete.

<table>
<thead>
<tr>
<th>Description of river current</th>
<th>Approximate current velocity of river ft./min</th>
<th>Approximate time in which mixing with sewage becomes complete</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very rapid</td>
<td>100 or more</td>
<td>5-1 min</td>
</tr>
<tr>
<td>Rapid</td>
<td>60-100</td>
<td>20-10 min</td>
</tr>
<tr>
<td>Moderate</td>
<td>40-60</td>
<td>90-30 min</td>
</tr>
<tr>
<td>Slow</td>
<td>20-40</td>
<td>3-2 h</td>
</tr>
<tr>
<td>Sluggish to very sluggish</td>
<td>20 or less</td>
<td>6-3 h</td>
</tr>
</tbody>
</table>

(Note that 88 ft./min = 1 m.p.h.)

* Assuming that 1 ft.\(^3\) = 0.2208 Imperial gallons.
A discussion of methods for the measurement of large flows of sewage and trade wastes by means of flow meters, weirs and flumes is beyond the scope of this book and the reader is referred to papers on the subject in the literature

A convenient way of measuring approximately very small flows of sewage or trade waste, say less than about 20 gal./min, is to procure a drum of about 10 gal. capacity, measure its volume by filling with a gallon jug, and determine with a stop-watch the time required to fill the drum.

The volume of a factory effluent can usually be obtained from the works manager and can often be estimated from a knowledge of the water consumption.

PHYSICAL METHODS

A discussion of physico-chemical methods with full details of their practical application to all kinds of problems is given in the standard works by Reilly and Rae, and Gibb, to which the reader is referred for further information.

TEMPERATURE

It is usually sufficiently accurate to take the temperature of a stream water or an effluent to the nearest half degree centigrade. For more accurate work, especially in connection with the calculation of the percentage saturation of dissolved oxygen, a standardized thermometer graduated in tenths of a degree centigrade should be used.

COLOUR

The purest natural river waters are generally colourless and the presence of any colour at all is usually an indication of the presence of organic matter, which may impart a straw, yellow or brownish tint to the water. It is possible in these cases to express the colour in terms of the Hazen standard unit, i.e. the colour given by 1 p.p.m. of platinum in the form of chloroplatinic acid modified by the addition of 2 p.p.m. of cobaltous chloride hexahydrate.

This determination is much simplified by using the B.D.H. Lovibond neslerizer and a disc with nine permanent glass standards ranging from 5 to 70 Hazen units. If much suspended matter is present, the estimation of colour should be made after settlement or centrifuging.

With many polluted waters containing highly coloured wastes (e.g. textile dye wastes), the colour may be green, blue, purple, black, etc., and so cannot be determined by the simple procedure
DETECTION AND MEASUREMENT

just outlined. In such cases, use can be made of the Lovibond tintometer in which the colour is matched by a suitable combination of graded red, yellow, and blue glass filters and expressed in terms of the internationally used Lovibond units.

Runcorn and Hayton43, 46 have described accurate spectrophotometric and filterphotometric methods of determining colour in waters and industrial wastes in terms of the dominant wavelength (which defines the hue or kind of colour), luminance (which defines the degree of brightness) and purity (which defines saturation, i.e. pastel, pale, etc.). The procedure is given in the latest edition of the A.P.H.A. Standard Methods2. For most purposes, however, it is sufficient to express the colour of a river water or trade waste in purely qualitative terms.

TURBIDITY OR TRANSPARENCY

Various commercial turbidimeters, visual and photoelectric, are available for the measurement of turbidity and they are generally calibrated against standards made up from fuller's earth, a correction being made for any colour in the sample. In the U.S.A., the unit of turbidity was, until recently, the turbidity imparted to a water by 1 p.p.m. of fuller's earth. This unit has now been abandoned in favour of arbitrary turbidity units fixed in relation to a standard Jackson candle turbidimeter. This change has evidently been made because, as experience in this country also shows, standards prepared from fuller's earth vary somewhat with the source and grade of material used and so do not give reproducible results.

A submersible photoelectric absorptiometer specially suitable for the measurement of high turbidities in river waters was used in the survey of the Thames estuary by Scruggs, Briggs and Knowles47. To obtain the calibration curve, the instrument was placed in water free from turbidity (i.e. water of 100 per cent transmission) and by the use of various neutral density filters, dial readings were obtained corresponding to a particular optical density or percentage transmission. Curves showing the relation between the optical density and various types of suspended matter of different nature and particle size were also constructed.

The use of the Zeiss-Pulfrich nephelometer for determining the turbidity of river waters has been described by Rms48.

For rapid routine work, an inexpensive visual apparatus for measuring approximately the clarity or transparency of a sample (which is inversely related to its degree of turbidity) can be constructed from a colourless glass tube, 2 ft. long, and of internal diameter about 1 in. with a plane glass bottom on the outside of
which a black cross (with lines 1 mm in width) is pasted. A side tube near the bottom connects, via rubber tubing, with a glass reservoir, and the depth of liquid in the tube is adjusted by raising or lowering the reservoir until on looking down the tube, preferably in north daylight, the black cross just disappears from sight. The length of the liquid column in millimetres is measured or read off from graduations on the tube. If the test is performed on the settled as well as shaken sample, the difference gives a good idea of the amount of suspended matter present. With good effluents or river waters, the black cross may still be visible even at a depth of 600 mm, in which case the result is recorded as >600 mm. Most satisfactory sewage effluents and good trade effluents give settled transparency figures of 300 mm or more. Poorly clarified sewage or trade effluents may give readings of less than 100 mm.

**pH Value**

Wide-range and narrow-range test-papers for the approximate estimation of pH values ranging from 2·0 to 10·5 are available commercially.* These papers are convenient for rough work and for field tests. The use of the British Drug Houses universal indicator is also convenient for obtaining an approximate idea of the pH value of a sample, the colour obtained at various pH values being indicated in Table 50.

### Table 50. Colours obtained at various pH values with B.D.H. universal indicator

<table>
<thead>
<tr>
<th>pH value</th>
<th>Colour</th>
<th>pH value</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>3·0</td>
<td>Red</td>
<td>8·0</td>
<td>Green</td>
</tr>
<tr>
<td>4·0</td>
<td>Deeper red</td>
<td>8·5</td>
<td>Bluish-green</td>
</tr>
<tr>
<td>5·0</td>
<td>Orange-red</td>
<td>9·0</td>
<td>Greenish-blue</td>
</tr>
<tr>
<td>5·5</td>
<td>Orange</td>
<td>9·5</td>
<td>Blue</td>
</tr>
<tr>
<td>6·0</td>
<td>Orange-yellow</td>
<td>10·0</td>
<td>Violet</td>
</tr>
<tr>
<td>6·5</td>
<td>Yellow</td>
<td>10·5</td>
<td>Reddish-violet</td>
</tr>
<tr>
<td>7·0–7·5</td>
<td>Greenish-yellow</td>
<td>11·0</td>
<td>Deeper reddish-violet</td>
</tr>
</tbody>
</table>

More accurate determinations of pH (usually to within 0·1 pH unit over the range 0·2–10·0) can be made with the Lovibond comparator† in which, with the aid of a series of suitable discs, the colour obtained with 10 ml. of sample plus an appropriate amount of a suitable indicator (usually 0·5 ml.) is matched against Lovibond permanent glass colour standards. With many pure river waters and other samples which are poorly buffered (e.g. samples having a

* For instance from the British Drug Houses, Poole, Dorset; and from Johnsons, Hendon, London, N.W.4.
† Obtainable from The Timometer Ltd., Salisbury, or from the British Drug Houses, Poole, Dorset.
DETECTION AND MEASUREMENT

methyl orange alkalinity, expressed as CaCO₃, of less than about 20 p.p.m., an appreciable error can be introduced due to the pH value exerted by the indicator itself. In such cases, it is preferable to use the B.D.H. Lovibond nesslerizer in which 50 ml. Nessler tubes replace the 10 ml. tubes of the comparator and a much smaller proportion of indicator solution (0.2 ml.) is taken. With this instrument, the colour is matched looking vertically down the column of liquid and not, as in the case of the comparator, horizontally through the liquid. Some useful indicators suitable for use with these two instruments are given in Table 51.

Table 51. Selected list of indicators suitable for the colorimetric determination of pH in the range 0.2–14.0 with the Lovibond comparator or the B.D.H. Lovibond nesslerizer

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range of colour disc (in steps of 0.2 unless otherwise indicated)</th>
<th>Instrument</th>
<th>Colour change</th>
<th>pH range of indicator</th>
</tr>
</thead>
<tbody>
<tr>
<td>C. cresol red (acid range)</td>
<td>0.2–1.0</td>
<td>C</td>
<td>red-Orange—yellow—</td>
<td>acid-alkaline</td>
</tr>
<tr>
<td>Thymol blue (acid range)</td>
<td>1.2–2.8</td>
<td>C</td>
<td>purple-Red—orange—yellow—</td>
<td></td>
</tr>
<tr>
<td>Bromophenol blue</td>
<td>2.8–4.4</td>
<td>C</td>
<td>yellow—purplish—grey—purple—blue</td>
<td></td>
</tr>
<tr>
<td>B.D.H. '3061' indicator</td>
<td>3.0–4.6</td>
<td>C, N</td>
<td>purple—grey—green</td>
<td></td>
</tr>
<tr>
<td>Bromocresol green</td>
<td>3.6–5.2</td>
<td>C</td>
<td>yellow—green—blue</td>
<td>acid—alkaline</td>
</tr>
<tr>
<td>B.D.H. '4460' indicator</td>
<td>4.4–6.0</td>
<td>C</td>
<td>red—orange—yellow—green—</td>
<td></td>
</tr>
<tr>
<td>Bromocresol purple</td>
<td>5.2–6.8</td>
<td>C</td>
<td>yellow—green—</td>
<td>acid—alkaline</td>
</tr>
<tr>
<td>Bromothymol blue</td>
<td>6.0–7.6</td>
<td>C</td>
<td>yellow—green—blue</td>
<td>acid—alkaline</td>
</tr>
<tr>
<td>C. cresol red (alkaline range)</td>
<td>7.2–8.8</td>
<td>C, N</td>
<td>yellow—orange—pink—violet—red—blue—</td>
<td></td>
</tr>
<tr>
<td>Thymol blue (alkaline range)</td>
<td>8.0–9.6</td>
<td>C</td>
<td>yellow—greenish—</td>
<td>acid—alkaline</td>
</tr>
<tr>
<td>B.D.H. '9010' indicator</td>
<td>8.6–10.0</td>
<td>C</td>
<td>yellow—orange—pink—red—</td>
<td></td>
</tr>
<tr>
<td>B.D.H. '9011' indicator*</td>
<td>9.0–11.0</td>
<td>C, N</td>
<td>yellow—grey—green—brownish—grey—pink—orange</td>
<td></td>
</tr>
<tr>
<td>B.D.H. '1014' indicator†</td>
<td>11.0–14.0</td>
<td>C, N</td>
<td>green—brownish—grey—pink—orange</td>
<td></td>
</tr>
</tbody>
</table>

* 5 standards in steps of 0.5.
† 9 standards in steps of 0.5. Unsuitable in presence of lime.

The colorimetric determination of pH can also be carried out accurately by comparing the colour produced by the sample plus a specified amount of indicator with that of buffer solutions of known
pH containing the same amount of indicator. Lists of suitable indicators are given by Snell, Bartrum and Tomicka.

When samples are coloured or very turbid, and generally when greater accuracy is required, the electrometric method utilizing the glass electrode is to be preferred. The calibration of the glass electrode is carried out using buffer solutions whose pH value is known with a high degree of accuracy. Table 52 gives the pH values of aqueous solutions of standards that have been recommended for this purpose.

Table 52. Calibration of glass electrode for pH determinations: pH values of standard solutions at various temperatures (°C)

| Standard substance | Formula | Composition of solution w = Molar | pH | Refere-
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>w = Molar H2O</td>
<td>15°</td>
<td>20°</td>
</tr>
</tbody>
</table>
| Potassium tetroxa
date | KH2C2O4·2H2O | 0.1 w | 52, 55|
| Potassium tetroxa
date | KH2C2O4·2H2O | 0.01 w | 52, 55|
| Potassium bitartrate | K2C4H4O6 | Saturated | 56, 57|
| Potassium hydrogen phthalate | C4H4O6 | 0.05 w | 52, 57|
| Borax | Na2B4O7·10H2O | Saturated | 56|
| Lanthum carbonate | La2(CO3)3 | Saturated | 56|
| Trisodium phosphate | Na3PO4 | 0.01 w | 57|

Oil and other immiscible liquids

According to Kirschenman and Pomeroy, oil is the 'relatively non-volatile liquid component that contributes to the formation of oil films and deposits'. This definition excludes oils that evaporate rapidly at ordinary temperatures; such oils are usually of minor importance in river pollution since owing to their volatility they do not contribute to the formation of oily films on the surface of a stream. In the normal procedures for determining oil based on extraction with a volatile solvent and evaporation of the extract, volatile oils would, of course, not be included since they would be lost by volatilization.

Oil is usually determined by extracting the acidified sample with a suitable organic solvent (e.g. light petroleum, hexane, ethyl ether, or chloroform), removing the solvent from the extract by evaporation or distillation, drying the residual oil at 100-105°C, and weighing. The method is only approximate since it gives not only oil but also fat, tar, and any grease associated with the suspended solids. Kirschenman and Pomeroy describe a wet extraction procedure for determining oil in oilfield waste waters using commercial...
DETECTION AND MEASUREMENT

hexane as solvent; the latter was removed by distillation on the water-bath and the oil obtained was finally dried at room temperature. More reproducible but slightly lower results were obtained by these authors by a flocculation method using zinc acetate and sodium carbonate, the precipitated zinc carbonate trapping the oil very effectively; after filtering and air-drying the precipitate, the adsorbed oil was extracted with hexane. Small amounts of oil can be estimated by flocculation with iron salts. Ferric chloride is added to the sample which is then heated to boiling and precipitated with ammonia. The precipitated ferric hydroxide, which entrains all the oil, is filtered, washed with water and dried, and the oil is then extracted from the precipitate with ether.

Pringle has described a method suitable for very small quantities (up to 10 p.p.m.) of oil. The sample (24 litres) acidified with hydrochloric acid is shaken with benzene and to prevent emulsion formation hydrogen is generated by introducing magnesium wire. The benzene layer is distilled and the residual oil is dried at 100°C.

Pomeroy has devised a useful test for the estimation of the floatable oil and grease present in waste waters discharging to sewers. The estimation of very slight traces of oil is difficult by ordinary methods but Holloxender has determined as little as 0.02 p.p.m. of oil in steam condensate by comparing the fluorescence under ultra-violet light with that of standards.

Oil often consists of motor fuel oil or lubricating oil derived from petroleum. Such oils dissolve in light petroleum giving a brown solution exhibiting a greenish fluorescence. Standard methods for testing such oils are given in a recent publication; important characteristics of these oils are specific gravity, distillation range, flash point, viscosity, and behaviour on heating and ignition. If coal-tar oils are present, they should show the special reactions for phenols (cf. page 322) and will give a strong phenolic odour on ignition.

ELECTRICAL CONDUCTIVITY

Gustafson and Behman have recommended the determination of electrical conductivity as a rapid means of checking results of the determination of total dissolved solids as obtained by the evaporation method which is often slow and not always very accurate owing to losses of certain mineral constituents. It may be necessary to dilute the sample first and it is essential to remove any free carbon dioxide by aeration with air free from carbon dioxide.

Although the determination of electrical conductivity is useful in the analysis of potable waters in showing changes in the concentration of total ionizable salts, its application to river survey work is
somewhat limited. Nevertheless, it can be used to indicate altera
tions in the content of ionizable salts in river waters due to such dis­
charges as brine, oil-field waste waters, and chemical wastes. A
convenient commercial instrument (the dionic water tester*) is
available for this purpose and this can easily be checked from time
to time against a standard solution of potassium chloride.

The unit used for expressing conductivity is the reciprocal of
1 megohm per centimetre-cube. Results should be corrected to a
standard temperature (generally 20° or 25° C). Conductivity in­
creases very markedly with rise in temperature, usually approxi
mately 2 per cent per degree centigrade.

MACHERETH66A has made use of determinations of electrical con­
ductivity for measuring the cation concentration (Ca, Mg, Na and
K) and the anions of strong and weak acids in diluted river waters
after the latter have been passed through columns of strongly basic
and acidic ion exchange resins.

SUSPENDED SOLIDS, DISSOLVED SOLIDS AND TOTAL
SOLIDS†

Two standard methods are in use in this country for the determina­
tion of suspended solids.

The Gooch crucible method involves the filtration by suction of
a known volume of the shaken sample through a specially prepared
asbestos mat in a Gooch crucible, which is then dried at 100-105° C.
The preparation of a series of such crucibles for routine work is
rather laborious and filtration is sometimes very slow particularly
with polluted samples containing much colloidal matter and greasy
suspended matter.

In the alternative centrifuge method, which the writer prefers, a
known volume of the shaken sample (usually 50-200 ml.) is centri­
fuged under standardized conditions using special conical-end
centrifuge tubes. After pouring off the separated liquid, the sus­
pected matter at the bottom of the tubes is washed with distilled
water, re-centrifuged, the separated water is again removed, and the
suspended matter is transferred to a weighed platinum or other
suitable basin by means of a jet of water from a wash bottle and
dried at 100-105° C. In general, this method is much quicker
than the Gooch crucible method, especially when large numbers of
samples are being examined, but gives slightly lower results as it
does not include any colloidal matter that tends to be retained by
the Gooch mat. Indeed, the work of RUDOLFS and BALMAT67 has
definitely shown that the so-called 'suspended solids' determination

† See references 1-3, 12, 14.
as carried out by the filtration of raw sewage through a Gooch crucible does include a portion of the colloidal fraction. Another advantage of the centrifuge method lies in the ease with which a determination of volatile solids can be subsequently carried out by ignition of the platinum basin containing the suspended solids; during this ignition, valuable information about the nature of the suspended solids can be obtained by noting any blackening, darkening or colour changes, any odours produced, evolution of fumes, appearance of sparks, flame, etc. The mineral residue remaining after ignition should be subjected to a qualitative analysis for the commoner cations and anions, especially calcium, magnesium, iron, chromium, copper, zinc, lead, sulphate, chloride and phosphate.

The filtrate from the Gooch crucible, or the separated liquid in the centrifuge, can be used for a determination of 'dissolved solids' or 'soluble solids' by evaporating a known volume to dryness. Any colloidal matter present will also be included in this determination.

Total solids can be determined by evaporating a known volume of the well-shaken sample to dryness on the water bath and drying at 100–105 °C. In the case of potable waters, however, it is customary in this country to dry at 180 °C, since at this temperature calcium sulphate is anhydrous and magnesium sulphate contains one molecule of water of crystallization. When hygroscopic salts (e.g. calcium and magnesium chlorides and nitrates) are present, the final weighing is likely to be somewhat inaccurate.

**RADIOACTIVITY**

The detection and measurement of radioactivity require the use of specialized and expensive equipment as well as staff specially trained for the purpose. Commercial instruments are now available which permit the detection of α-, β- and γ-radiation. Since some form of protection is necessary for personnel handling radioactive wastes, a radiological laboratory must include a number of special features not to be found in an ordinary laboratory. The testing of radioactive effluents in this country is at present in the hands of the Ministry of Housing and Local Government, and it is unlikely that for some considerable time river boards, sewage works or trade premises will be called upon to determine radioactivity. The reader who is interested in radioactive techniques and in the design of radiological laboratories is referred to the extensive literature on the subject. (See references 68–71, 72.)

**FROTHING TEST**

As already explained in Chapter 3 (page 41), the growing use of synthetic detergents for domestic and industrial purposes is causing
considerable froth to appear on the surface of many rivers in this country. It is very desirable, therefore, to have some test which can be used to determine the extent to which a river water shows a tendency to froth when shaken or aerated.

A simple empirical test of this kind is in use in the laboratories of the Mersey River Board. A 48-oz. or 50-oz. glass-stoppered bottle of colourless glass is half filled with the sample, shaken vigorously for 30 sec, and the breaking time of the froth noted as well as observations on the time taken for large bubbles, fine scum and all other bubbles to disappear.

<table>
<thead>
<tr>
<th>Description of water</th>
<th>Remarks on froth</th>
<th>Breaking time of froth</th>
<th>Time taken for large bubbles to disappear</th>
<th>Phantom froth (fine scum)</th>
<th>Approx. time for total disappearance of all bubbles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-frothy.</td>
<td>—</td>
<td>nil</td>
<td>up to 3 sec</td>
<td>nil</td>
<td>up to 3 sec</td>
</tr>
<tr>
<td>Almost non-frothy</td>
<td>—</td>
<td>up to 1 sec</td>
<td>3 to 5 sec</td>
<td>slight trace</td>
<td>1 h</td>
</tr>
<tr>
<td>Slightly frothy</td>
<td>—</td>
<td>up to 10 sec</td>
<td>up to 30 min</td>
<td>trace</td>
<td>4 h</td>
</tr>
<tr>
<td>Rather frothy</td>
<td>1 in. or about 5</td>
<td>—</td>
<td>—</td>
<td>1/4 of surface still</td>
<td>1/4 of surface still covered in 18 h</td>
</tr>
<tr>
<td>Frothy</td>
<td>1/4 in. layer</td>
<td>2 to 4 h</td>
<td>—</td>
<td>—</td>
<td>1/4 of surface still covered in 18 h</td>
</tr>
<tr>
<td>Very frothy</td>
<td>1 in. layer</td>
<td>18 h or more</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

The first two waters (non-frothy and almost non-frothy) are unlikely to cause foaming troubles to river water users.

Table 53 shows a classification of river waters based upon this test and used in the Mersey River Board laboratories. It is found in practice that those river waters belonging to the categories of 'non-frothy' and 'almost non-frothy' do not cause foaming troubles or give rise to complaints of froth.

**OTHER PHYSICAL METHODS**

Many instrumental methods\textsuperscript{13}-\textsuperscript{15} are finding increasing application in pollution problems in cases where purely chemical methods have hitherto been used. Some of the more important of these newer techniques will now be briefly discussed.
DETECTION AND MEASUREMENT

Chromatography

This is a method of separating substances (especially mixtures of complex closely related organic materials) by passage of the sample in a suitable solvent through a vertical column of an adsorbent (generally alumina). After washing with the pure solvent, there will be a series of zones ranging from the most easily adsorbed compounds at the top to the least adsorbed substances towards the bottom. After drying the column by gentle suction with a water pump, the zones are isolated by cutting and are then extracted ('eluted') with a suitable solvent.

Chromatography was used by Wedgwood and Cooper for separating traces of polynuclear hydrocarbons (e.g. pyrene, fluoranthene, and 3:4-benzpyrene) in sewage, sewage humus, and industrial effluents. The hydrocarbons were subsequently identified and determined by absorption spectroscopy (see under Hydrocarbons, page 328; also references 314–316A).

Absorption spectroscopy

It is possible to measure the optical density of a substance at different wavelengths, generally in the ultra-violet region, by using a spectrophotometer. The absorption spectrum, or curve obtained by plotting wavelengths against optical density, often shows well-defined maxima and minima which may be characteristic of the absorbing substance and so be of value not only in its identification but also, by application of the Beer–Lambert law, in its quantitative determination.

Emission spectroscopy

It has long been known that an element yields a characteristic emission spectrum which affords a good criterion of the identity of the element in question. The spectrum can be a flame, arc, or spark spectrum, and the intensity of the spectral lines on a photographic plate depends upon the quantity of the element present. This intensity can be measured by means of a microphotometer, or visually by comparison with standard spectra in a series containing known and gradually increasing amounts of the element to be determined. The method is particularly useful for determining traces of the alkali metals (e.g. sodium and potassium) and the alkaline earth metals (e.g. calcium, strontium and barium) for which suitable chemical methods are scarce and lacking in sensitivity and specificity.

Flame photometry

In this comparatively recent technique, the sample solution is
atomized, sprayed into a specially designed burner, and the intensity of the light emitted by a particular spectral line is measured with the aid of a suitable light filter, a photoelectric cell and a galvanometer. Commercial instruments for the determination are available at a reasonable price, and the method is a particularly useful and rapid one for traces of sodium and potassium.

**Polarography**

Polarographic procedures are particularly useful for the simultaneous determination of small amounts of metallic ions for which diffusion current-voltage curves are obtained using a cell containing mercury as anode and a cathode consisting of a dropping mercury electrode (i.e. a glass capillary tube from which a drop of mercury falls about once every few seconds). In the presence of a sample containing several metals of different reduction potential, a series of steps is obtained on the curve, the voltage indicating the particular metal and the height of the step indicating the concentration of the metal.

The method has been applied by Butts and Mellon to the determination of metals in industrial wastes but is restricted to metal concentrations down to about 3–5 p.p.m. and consequently is not so sensitive as most colorimetric procedures.

**Physical titration methods**

Titrations by instrumental methods frequently have advantages over the ordinary chemical titrations when indicators fail to give satisfactory results, for instance in many oxidation-reduction titrations and when highly coloured solutions are being tested.

In potentiometric titrations, the equivalence point is indicated by an abrupt change in potential when the E.M.F. is plotted against the volume of titrant.

In conductometric titrations, the end-point is shown by a sudden change in conductivity when the conductance is plotted against the volume of titrating solution.

In amperometric titrations, the end-point is indicated on a curve in which the current passing through the titration cell between a dropping mercury electrode and a standard calomel electrode is plotted against the volume of titrant.

Commercial apparatus is available for carrying out these various titrations.

**Oxidation-Reduction potential**

This has been fully discussed previously (see Chapter 6, pages 120–23).
The chemical methods used for the quantitative determination of pollution are mainly volumetric (titrimetric) and colorimetric; gravimetric methods involving the conversion of the constituent to be estimated to a suitable insoluble form for weighing (e.g. the determination of sulphate by precipitation as insoluble barium sulphate) are less frequently used on account of their tedious nature and much lower sensitivity (see references 13, and 81–98).

Volumetric methods, unlike gravimetric methods which are mainly confined to precipitation reactions, are applicable to almost every type of chemical reaction, for instance precipitation reactions, neutralizations, complex ion formation, and oxidation-reduction reactions. The sensitivity of volumetric methods is increased by the use of more dilute standard solutions (e.g. N/40, N/80, N/100 or even N/1000) than those generally employed in ordinary analysis. In some cases, for instance, the estimation of traces of ferrous iron by titration with N/1000 potassium dichromate (page 307), or the titration of cyanide with N/1000 silver nitrate in the modified Leibig method (page 320), the use of a micro-burette may be desirable to increase the accuracy. In these and similar cases indicator blanks should be determined experimentally using the reagents and distilled water instead of the sample and the appropriate correction made to the titration when the sample is being titrated.

Colorimetric methods are, in general, of a still higher order of sensitivity than volumetric methods. For example, as little as 0-01 p.p.m. of ammoniacal nitrogen can be estimated by means of the yellowish-brown colour given with Nessler’s reagent (page 283) whereas an ordinary titration method (page 283) can scarcely determine with accuracy less than 1 p.p.m. of ammoniacal nitrogen unless the specialized micro-diffusion techniques due to Conway21 are used.

A colorimetric method involves the determination of the concentration of a coloured substance in solution and this can be done either visually in Nessler tubes,* or photoelectrically by measuring the effect of the transmitted light on a photoelectric cell. The photoelectric procedure is theoretically more accurate but necessitates the use of an expensive instrument. Visual methods, involving comparison of the intensity of the colour of the unknown solution with that of the colour produced under the same conditions in a series of standard solutions in Nessler glasses, are in general satisfactory

* The use of the visual Duboscq colorimeter for this purpose has now become rare.
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for most colorimetric work, especially for occasional determinations. Where it is necessary to extract a coloured substance with an immiscible organic solvent, for instance in methods involving the use of carbon tetrachloride solutions of dithizone, it is preferable to use a photoelectric method as the extraction of a whole series of standards every time the determination is carried out is very tedious.

Although photoelectric methods have many advantages where large numbers of determinations are to be performed, for research work and in other cases where a high degree of accuracy is required, it must be remembered that they may be affected by errors due to impurities in every new batch of reagents, by mechanical and other defects in the apparatus, by fluctuations in temperature and in the mains voltage, and by any turbidity* or 'off-tints' in the solutions. In routine work, a limited staff does not always have the time needed to test and check the instrument or to prepare a new calibration curve frequently.

The preparation of a set of standards for a visual method can be avoided and much time saved by the use of permanent colour standards; discs containing a series of graded coloured glasses suitable for a particular determination have become very popular in recent years. Discs for most of the common colour tests are now available for use with either the Lovibond comparator (which utilizes 10 ml. tubes) or the larger B.D.H. Lovibond nesslerizer (which utilizes 50 ml. Nessler tubes). When using these visual instruments, it is essential that the method described in the Tintometer books should be precisely followed. It is desirable that with every new batch of reagents the colour discs should be checked against standards; this is not necessary when the ordinary standard series method is used since any errors due to impurities in the reagents are compensated for.

Important requirements for any reaction used in colorimetric analysis are that the reaction should be highly sensitive, specific, if possible, or at least fairly selective, and that the colour should be reasonably intense, stable, reproducible, and not too sensitive towards light, and finally it is desirable that the colour system should conform to Beer's law, i.e. the intensity of the colour should be proportional to the concentration of the substance being determined.

PREPARATION OF SAMPLE FOR ANALYSIS

No preliminary treatment is required for the sample in the case of such determinations as acidity, alkalinity, dissolved oxygen, suspended and total solids, and 3 minutes and 4 hours permanganate.

* Chamberlin has well said that 'no electronic device is capable of doing what the eye does, namely to separate out the difference between colour and turbidity.'
DETECTION AND MEASUREMENT

values. Such processes as centrifuging, or less satisfactorily filtration, may be desirable when the suspended solids content of the sample is sufficiently high to cause interference with colorimetric methods, for instance in determinations of pH, nitrite, nitrate, phenols and cyanides. When the sample is cloudy and coloured, clarification with aluminium hydroxide cream, or with aluminium sulphate and sodium carbonate, and colour removal with activated carbon, may be necessary. Distillation is sometimes used to separate volatile compounds from interfering substances, for example, in the determination of ammonia, phenols and hydrogen cyanide. When a method is not sufficiently sensitive, concentration of the desired constituent, if non-volatile, may often be achieved by evaporation of the sample. Extraction with an immiscible solvent (e.g. ether, chloroform, benzene, carbon tetrachloride, amyl alcohol) is another useful procedure for removing interfering substances and it finds application in the Fox-Gauge method for the determination of phenols where chloroform is used to separate vegetable phenolic bodies from tar acids (page 325). Ion exchange methods of separation have not often been used in the past but are finding increasing application; for instance an ion-exchange resin was used by Rush and Yoe275 (page 318) for the separation of zinc from interfering metals.

When metallic constituents are to be determined colorimetrically, it must be remembered that the metal may be present partly in solution and partly in the sediment. In such cases, the metal is determined in the centrifuged or settled sample and a second determination is performed on the shaken sample (i.e. the sample including its sediment). In the latter case, the sample is evaporated to dryness and ignited at a low red heat to destroy organic matter; the residue is treated with hydrochloric acid, again evaporated to dryness and heated to 105-110°C in the usual way to render any silica insoluble, and the metal finally extracted with hot hydrochloric acid. Alternatively, for greater accuracy, Butts, Gahler and Mellon220 recommend destruction of organic matter by evaporating the sample first with nitric acid to a small volume, then with a mixture of nitric and sulphuric acids until dense white fumes of sulphur trioxide appear. If lead is present, insoluble lead sulphate may separate out in the last procedure and can be dissolved in hot 40 per cent ammonium acetate. The destruction of organic matter in solid and semi-solid materials (e.g. river muds, sludges) can be carried out in a similar way. In the presence of difficulty oxidizable organic matter or when lead is to be determined, destruction of organic matter is best carried out with nitric and perchloric acids.220

When total chromium is to be determined in a sample containing
both trivalent chromium and hexavalent chromium, there may be loss of chromium as volatile chromyl chloride if the sample contains chloride and is evaporated with sulphuric acid. In such cases, pretreatment with sodium sulphite and sulphuric acid is necessary to reduce chromate to chromic sulphate.229.

A sample containing ferrous iron must not, of course, be evaporated or treated with any oxidizing reagent, otherwise oxidation to the ferric state will take place (see page 305).

**ALKALINITY AND ACIDITY**

Alkalis are present in kier liquors from cotton mills and paper works, in wool scouring wastes and many chemical wastes. Acids occur in iron and copper pickle liquors, in drainage from coal mines and coal tips, in some chemical wastes, and in waste waters from the manufacture of explosives. (Although the determination of pH value (page 260) gives information about the intensity of the alkalinity or acidity, a titration method is required to estimate the actual amount of alkali or acid present.)

If the pH value of the sample is greater than 8.3, carbonate alkalinity or caustic alkalinity is present, and this is determined by titration with N/10 hydrochloric or sulphuric acid using phenolphthalein or any of the alternative indicators shown in **Table 54**.

<table>
<thead>
<tr>
<th>Indicator</th>
<th>pH range</th>
<th>Colour change</th>
<th>Acid</th>
<th>Alkaline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phenolphthalein</td>
<td>8.3-10.0</td>
<td>Colourless</td>
<td>Pink</td>
<td></td>
</tr>
<tr>
<td>e- cresolphthalein*</td>
<td>8.2-9.8</td>
<td>Colourless</td>
<td>Purple-red</td>
<td></td>
</tr>
<tr>
<td>Thymol blue</td>
<td>8.0-9.6</td>
<td>Colourless</td>
<td>Blue</td>
<td></td>
</tr>
<tr>
<td>Ethyl blue-iso-dinitrophenyl acetone*</td>
<td>7.5-9.2</td>
<td>Colourless</td>
<td>Blue</td>
<td></td>
</tr>
<tr>
<td>Tetrachlorophenolphthalein*</td>
<td>8.2-9.4</td>
<td>Colourless</td>
<td>Pink</td>
<td></td>
</tr>
</tbody>
</table>

*Somewhat more sensitive than phenolphthalein.  
*Suitable for orange or red solutions.  
*Useful if hypochlorite is present. The pink colour of phenolphthalein in alkaline solution is bleached by chlorine.

If the pH value of the sample lies between 4.0 and 8.3, bicarbonate alkalinity is present and may be determined by titration with N/10 hydrochloric or sulphuric acid, using methyl orange or one of the other indicators listed in **Table 55**.

A sample with a pH value of less than 4.0 contains, in general, mineral acid, the amount of acid present being determined by titration with N/10 sodium hydroxide, using methyl orange or one
DETECTION AND MEASUREMENT

of the indicators listed in Table 55. If organic acids are present, the methyl orange end-point will be somewhat indefinite, and the acidity to phenolphthalein should then be determined.

Table 55. Indicators suitable for determination of mineral acidity, or of bicarbonate alkalinity

<table>
<thead>
<tr>
<th>Indicator</th>
<th>Useful pH range</th>
<th>Colour change</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methyl orange</td>
<td>2.9-4.6</td>
<td>Orange-red</td>
</tr>
<tr>
<td>Methyl orange-xylen cyanole*</td>
<td>2.9-4.6</td>
<td>Yellow</td>
</tr>
<tr>
<td>Bromphenol blue</td>
<td>2.8-4.6</td>
<td>Violet</td>
</tr>
<tr>
<td>Tetra bromophenol-tetra bromo methyl phthalein **</td>
<td>3.0-4.6</td>
<td>Blue</td>
</tr>
</tbody>
</table>

* Screening with the dye makes the methyl orange end-point more distinct, especially in artificial light.
** Useful as a substitute for free chlorinated or hypochlorite, which bleach the other indicators.

DISSOLVED OXYGEN

The dissolved oxygen content of a river water can be expressed in any of the following ways:

(i) parts by weight of oxygen per 100,000 parts by volume of sample (i.e. mg per 100 ml. or parts per 100,000);

(ii) parts by weight of oxygen per million parts by volume of sample (i.e. mg per litre or p.p.m.);

(iii) ml. (or c.c.) of oxygen (at 0° C and 760 mm of mercury pressure) per litre of sample (i.e. ml. per litre); and

(iv) as a percentage of saturation, in relation to the maximum amount dissolved by water at the same temperature and chlorinity as the sample. It is necessary, for this purpose to know the solubility of oxygen at various temperatures and salinities, and this is given in the Appendix, Table 107, page 577.

The following formulae show the relation between these various ways of expressing dissolved oxygen:

(a) parts per 100,000 of dissolved oxygen \( \times 10 = \) p.p.m. of dissolved oxygen

(b) ml. of dissolved oxygen per litre \( \times 1.43 = \) p.p.m. of dissolved oxygen

(c) p.p.m. of dissolved oxygen \( \times 0.7 = \) ml. of dissolved oxygen per litre

(d) dissolved oxygen, per cent of saturation

p.p.m. of dissolved oxygen found experimentally in sample \( \times 100 \) p.p.m. of oxygen under observed conditions of temperature and salinity obtained from Table 107 in Appendix.
A review of various methods which have been used for determining dissolved oxygen in waters is given by the Water Pollution Research Laboratory. The most accurate titration method for the determination of dissolved oxygen is that due to Winkler and generally carried out in glass-stoppered bottles completely filled with the sample in such a manner as to avoid aeration. Winkler’s method is based upon the formation of a white precipitate of manganous hydroxide by the action of alkaline potassium iodide on manganous chloride or sulphate and the conversion of this white precipitate by the dissolved oxygen to a brown precipitate of manganic hydroxide; the latter dissolves upon addition of sulphuric acid giving manganic sulphate which immediately liberates iodine from potassium iodide in amount equivalent to the quantity of dissolved oxygen originally present:

\[
\begin{align*}
\text{MnSO}_4 + 2\text{KOH} & = \text{Mn(OH)}_2 + \text{K}_2\text{SO}_4 \\
2\text{Mn(OH)}_2 + \text{O}_2 & = 2\text{MnO(OH)}_2 \\
\text{MnO(OH)}_2 + 2\text{H}_2\text{SO}_4 & = \text{Mn(SO}_4)_2 + 3\text{H}_2\text{O} \\
\text{Mn(SO}_4)_2 + 2\text{KI} & = \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{I}_2
\end{align*}
\]

The liberated iodine is then estimated by titration with a standard solution of sodium thiosulphate, using starch as indicator.

Several modifications of the Winkler method are used when interfering substances are present.

In the Rideal-Stewart, or permanganate modification, which is used when ferrous salts, sulphides, or nitrites are present, a preliminary oxidation of these interfering substances is carried out with potassium permanganate and sulphuric acid, the excess of permanganate being removed by addition of the minimum amount of potassium oxalate. In the presence of ferrous or ferric salts (e.g. stream water containing mine drainage), potassium fluoride should be added to form a complex iron fluoride which does not liberate iodine from potassium iodide, or alternatively the iron can be complexed by carrying out the final acidification with phosphoric acid instead of sulphuric acid.

When sulphites, thiosulphates and polythionates are present (e.g. in certain paper mill wastes), Theriault and McNamer recommend a preliminary oxidation for a few seconds with alkaline sodium hypochlorite to oxidize these sulphur compounds completely to sulphates; the excess of hypochlorite is then removed by acidification with sulphuric acid, treatment with potassium iodide and neutralization of the liberated iodine with sodium sulphite. The Winkler procedure is then followed, using a slight excess of the alkaline iodide reagent. The above procedure (omitting the treatment with alkaline hypochlorite) can also be used for samples containing hypochlorites or free chlorine.
When the only interference is due to nitrates, it is customary nowadays to use the simple azide procedure due to Alsterberg rather than the longer Rideal–Stewart method. In the azide method, nitrates are destroyed by addition of sodium azide (incorporated in the alkaline iodide reagent) which in the presence of sulphuric acid (used later for the acidification) reacts with nitrates according to the equations:

\[
2\text{NaN}_3 + \text{H}_2\text{SO}_4 = 2\text{HN}_3 + \text{Na}_2\text{SO}_4
\]

\[
\text{HNO}_2 + \text{HN}_3 = \text{N}_2 + \text{N}_2\text{O} + \text{H}_2\text{O}
\]

Sulphamic acid has also been suggested as a means of destroying nitrates but it has not come into general use.

The Winkler method has been adapted to semi-micro work and to micro-work by the use of small or very small sample bottles. Briggs and his co-workers have described a continuous recording apparatus for dissolved oxygen based on the Winkler method which is adapted to automatic working by determining the liberated iodine photometrically. A modification of the Winkler titration method was used by Truesdale and his associates in a recent re-determination of the solubility of oxygen in water when exposed to air. As a check on the accuracy of this titrimetric procedure, Wheatland and Smith have compared determinations of the dissolved oxygen content of waters using the Winkler method and a new gasometric reference method, and the values obtained by the two methods agreed remarkably well, the mean difference between the results by these two methods being only about 0.01 p.p.m. of oxygen.

Another titration method for dissolved oxygen, finding occasional application in field and control tests, is that due to Miller and depends upon the oxidation of ferrous salts at a high pH value to ferric salts, tartrate being present to prevent any precipitation of ferric hydroxide. The sample containing alkali, Rochelle salt, and a drop or two of an indicator (phenosafranine or methylene blue) is titrated with a standard solution of ferrous sulphate or ferrous ammonium sulphate until the colour of the indicator is discharged. Another method depending upon the oxidation of ferrous salts was originally described by Mouh and later modified by other workers. The method is based on the oxidation of ferrous hydroxide to ferric hydroxide by dissolved oxygen; the mixture of ferrous and ferric hydroxides is then dissolved in dilute sulphuric acid and the excess of unoxidized ferrous salt determined by titration with potassium permanganate.

Russian workers have described an interesting titration method for dissolved oxygen depending upon the oxidation of cerous hydroxide in alkaline medium to ceric hydroxide, which, after solution
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in acid, is determined by titration with standard ferrous ammonium sulphate using N-phenylanthranilic acid as internal indicator.

GAD uses a method based on the oxidation of manganous hydroxide to manganic hydroxide but avoids the use of expensive potassium iodide by dissolving the precipitate in a mixture of sulphuric acid and phosphoric acid and titrating the manganic sulphate with standard ferrous sulphate using diphenylamine as indicator.

Many colorimetric methods have been suggested for the estimation of dissolved oxygen. For example, amidol buffered to pH 5.1 gives a reddish colour with dissolved oxygen and this reaction has been made the basis for a colorimetric method by ISAACS, GILCREAS, and ELLIS, and a simple procedure for use as a field test has been given by ELLIS, WESTFALL, and ELLIS.

Various adaptations of the Winkler method to colorimetric work have been proposed. For instance, the intensity of the yellowish-brown colour of the iodine can be estimated by comparison with standards, and, for this purpose colour discs are available for use with the Lovibond comparator and the B.D.H. Lovibond nesslerizer. A highly sensitive colorimetric method for the determination of dissolved oxygen in water utilizes the yellow colour produced when manganic hydroxide, formed by the action of dissolved oxygen on manganous hydroxide, is treated with an acid solution of o-tolidine. The method will estimate accurately dissolved oxygen concentrations of the order 0.02-0.1 p.p.m. Interference by iron is prevented by using phosphoric acid in place of hydrochloric acid.

BANKS estimates traces of dissolved oxygen (as little as 0.007 p.p.m.) in boiler water by applying Winkler's method and measuring the liberated iodine absorptiometrically by means of the purple-red colour it gives with 3,3'-dimethyl-naphthidine in the presence of a sodium acetate buffer.

Electrical methods for the determination of dissolved oxygen involving the use of the dropping mercury electrode (polarography) have been proposed by several American workers (see references 126-9) but, despite the attraction of their possible use for continuously recording dissolved oxygen, they have not found favour in this country owing to various practical difficulties.

3 MINUTES AND 4 HOURS PERMANGANATE VALUES

The determination of the amount of oxygen taken up by a sample in 4 hours from a dilute sulphuric acid solution of N/80 potassium permanganate when maintained in a stoppered bottle at a temperature equals 26.7 °C but has been standardized by the Ministry at exactly 27 °C.
DETECTION AND MEASUREMENT

...ture of 80°F* is one of the most important tests used in this country for assessing the quantity of oxidizable matter in the sample. The test, which in the past has been called the '4 hours oxygen absorption' or more briefly the 'O.A.', is completed by adding excess of potassium iodide, which reacts with the unused permanganate to give iodine, and titrating the liberated iodine with standard sodium thiosulphate. A determination is also generally performed in 3 minutes. The significance of these two tests is discussed in Chapter 10.

In the presence of other oxidizing agents, for instance, free chlorine or hypochlorites, chromates, manganese dioxide (from some lime sludges), a low or even 'negative' result may be obtained. In such cases, a 'blank' determination is carried out with the sample + dilute sulphuric acid + potassium iodide in order to estimate the iodine equivalent of the oxidizing agent and so enable a correction to be applied. Interference due to the presence of iron salts (e.g. if mine water is present) is best circumvented by adding syrupy phosphoric acid just before the potassium iodide when a complex ferri-phosphate is formed which does not liberate iodine from potassium iodide. If nitrates are present, they will, of course, be included in the figure obtained for the permanganate value, but many workers have in the past corrected the result. If the permanganate value is corrected in this way, the fact should be stated.

In the determination of the McGowan strength figure of sewages, it should be remembered that the customary N/80 permanganate is replaced by N/8 permanganate which gives somewhat higher values than the weaker permanganate. There is no satisfactory way of converting N/80 values to N/8 values, for, as explained in Chapter 12, page 420, the factor 1.6 given in a former Ministry publication has been shown to be quite unreliable.

Waters having a high content of chloride tend to give high results with the Ministry acid permanganate test and Roberts has suggested that this interference is probably due to the action of the liberated chlorine on certain organic substances and not, as hitherto believed, to loss of chlorine. Roberts finds that errors due to the presence of chlorides can be very much reduced by substituting dilute phosphoric acid for the dilute sulphuric acid used in the test.

Niedercorn and his co-workers have proposed the use of a simple and rapid alkaline permanganate procedure (carried out for 10 minutes at room temperature) for determining the organic content of industrial wastes containing high and fluctuating concentrations of chlorides.
Hypochlorite Values (3 minutes and 4 hours)

These are determined in a somewhat similar manner to the corresponding permanganate values, the acid N/80 potassium permanganate being replaced by an N/80 solution of sodium hypochlorite. These determinations are mainly of importance in connection with problems involving the differentiation between animal pollution and vegetable pollution. Gibson, following up earlier work of Buu-Dien and Dixon and Jenkins, showed that the determination of the ratio hypochlorite value: permanganate value could sometimes be of real significance in tracing a source of pollution since this ratio was shown to be less than 1.0 for organic matter of vegetable origin and greater than 1.0 for organic matter of animal origin. The method is further discussed in Chapter 10, page 374.

Values Obtained by Using Other Oxidizing Agents

In addition to permanganate and hypochlorite, various other oxidizing agents have been proposed from time to time for assessing rapidly the organic content of a sample, for instance potassium dichromate (References 135-144), ceric sulphate, and potassium periodate. The most popular of these is potassium dichromate, the use of which has been the subject of rather voluminous literature in the U.S.A., where the test is now generally called the 'Chemical Oxygen Demand' or C.O.D. test. In the U.S.A., potassium dichromate has now replaced potassium permanganate as a chemical oxidizing agent for assessing organic pollution. However, in view of the fact that the dichromate method involves refluxing the sample with potassium dichromate in the presence of 50 per cent sulphuric acid, it is less suitable than the English permanganate method for routine determinations on large numbers of samples.

BIOCHEMICAL OXYGEN DEMAND (B.O.D.)

This test, the most important and widely used of all tests for organic pollution, is normally carried out for routine work by the 'dilution' method, which was originally described in the 8th Report of the Royal Commission on Sewage Disposal, and has since undergone certain modifications in the interests of ease of performance, elimination of interferences, and accuracy. In outline, the test is carried out by preparing a suitable dilution of the sample with aerated water and dividing between two glass-stoppered bottles; the dissolved oxygen is determined at once on one bottle, and again when the second bottle has been incubated at a standard temperature for 5 days. The B.O.D., expressed in p.p.m., is the amount
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of oxygen in milligrammes taken up during the 5-day period by 1 l. of the sample. The dilution should be such that only about 50 per cent of the dissolved oxygen is taken up, therefore, with unknown samples several different dilutions should be prepared. The standard temperature originally selected by the Royal Commission146 was 65°F (=18.3°C) because it was unusual in this country for a river water in a non-manufacturing district to exceed this value even during the summer months. The Ministry of Housing and Local Government132 have, however, now recommended that the incubator temperature for the B.O.D. test should be 20°C. The Ministry1 have also recommended the use of a synthetic dilution water (distilled aerated water plus nutrient salts) in place of the aerated tap water hitherto used for dilution purposes, and this should result in better agreement in values obtained in different laboratories.

The azide modification147-149 for the estimation of the dissolved oxygen is now used wherever possible in B.O.D. determinations but the older Rideal-Stewart modification should be employed when ferrous salts are present (cf. under Dissolved Oxygen, page 274).

A useful check on the accuracy of the B.O.D. technique can be obtained by carrying out determinations on suitable standard organic compounds for which purpose Sawyer and his co-workers150 recommend glucose and glutamic acid (see page 383). Data on the B.O.D. of a number of pure organic compounds are given in a report of a research committee of the Federation of Sewage and Industrial Wastes Associations150A.

The occurrence of nitrification during the B.O.D. test (i.e. bacterial oxidation of ammonia to nitrite and nitrate) can cause abnormally high B.O.D. values. This can be prevented either by flash pasteurization, or by acidification to pH 3-0 followed by neutralization; the sample must then be seeded with fresh settled sewage (free from nitrifying bacteria) to supply the necessary organisms (see Chapter 10, page 384).

The seeding of river waters, sewages, or sewage effluents is not usually necessary when carrying out a B.O.D. determination since the right types of bacteria should normally be present. In the case of trade wastes, however, care must be taken to see that they are neutralized, if necessary, and seeded with settled sewage or river water. According to the A.P.H.A. Standard Methods5, the dilution should be such that the toxicity is removed and the maximum B.O.D. value obtained, but in practice this is not always feasible and some wastes will yield abnormally low values. Moreover, certain trade wastes containing toxic substances (e.g. phenols) may require specialized flora (not necessarily present in sewage) in order to get a true B.O.D. value but the use of properly...
acclimatized seeds for such wastes, although recommended by some workers\textsuperscript{150}, presents practical difficulties for routine work in laboratories dealing with a great variety of samples. In all B.O.D. work with trade wastes, many of which are deficient in nitrogen, phosphorus and other nutrients, care must be taken to ensure that sufficient nutrient materials are present (cf. page 386).

For research purposes, manometric methods (see references 151-7) have much to commend them and a tentative method using the manometric technique is given in the latest edition of the A.P.H.A. Standard Methods\textsuperscript{2}.

\textbf{Bryan and Rohlich}\textsuperscript{158} determine a 'chlorate oxygen demand' by incubating sewage for 5 days with excess of sodium chlorate, which is biochemically reduced to chloride equivalent to the oxidizable matter originally present. The 'chlorate oxygen demand' can be calculated from the difference between the final and initial chloride concentrations.

\textbf{Organic Carbon}\textsuperscript{1, 2, 3, 159}

The determination of total organic carbon affords at first sight an attractive method of assessing the amount of organic or carbonaceous impurity in a sample. In practice, however, the method has its limitations in view of the following considerations:

(a) The procedures for organic carbon are tedious and time-consuming, requiring the use of a train of apparatus taking up considerable bench space, and necessitate the adoption of elaborate precautions in the presence of interfering substances (e.g. carbonates, oxalates, thiocyanates, volatile organic substances, etc.). Since only one determination at a time can be carried out, the method is only of value for research work and is unsuitable for routine work.

(b) The total amount of organic carbon is of lesser importance in pollution work than that portion of the carbonaceous matter which is relatively easily oxidized biologically by microorganisms and which is much more simply evaluated by a B.O.D. test.

The majority of methods for the estimation of organic carbon in sewage and effluents involve the wet oxidation of the sample by a mixture of chromic and sulphuric acids followed by the determination of the evolved carbon dioxide by a suitable gravimetric or volumetric procedure. For instance, \textit{Mills}\textsuperscript{160}, in his studies of mud obtained from river beds, absorbed the carbon dioxide in a solution of barium hydroxide and weighed the precipitated barium carbonate. \textit{Jenkins} and \textit{Roberts}\textsuperscript{161}, who describe a fairly
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A straightforward method for determining organic carbon in sewage liquors and sludge, passed the carbon dioxide through acidified potassium iodide (to remove chlorine) and then through a solution of barium hydroxide, the amount of unused baryta being determined by titration. Recovery of carbon from a number of pure substances tested by this method was greater than 95 per cent.

STABILITY

The stability of a sample of river water or effluent is the ability of the sample to maintain itself in an oxidized state when kept out of contact with oxygen or air in an incubator at a specified temperature. Several forms of incubator test have been described and the most useful include the following:

Simple incubator test\(^{162}\)

This involves incubation of the sample in a stoppered bottle (or bottle provided with a water seal) for 5 days at 80° F (26.7° C\(^*\)), the appearance and odour being then noted. A smell of hydrogen sulphide and/or a black precipitate (due to ferrous sulphide) shows that the sample is unstable. In cases of doubt, traces of hydrogen sulphide can be detected in the air in the upper part of the bottle by means of a slightly moistened lead acetate paper.

Scudder's permanganate incubator test\(^{162}\)

The 3 minutes acid permanganate value (corrected if necessary for nitrite) is determined on a sample before and after incubation for 5 days at 80° F (26.7° C\(^*\)). If this value increases (due to sulphide) after incubation (allowing, of course, for a small margin due to experimental error), the sample may be regarded as unstable.

Stoddart's incubator test\(^{163}\)

In this modification, the sample is incubated for 3-6 days and any hydrogen sulphide formed is detected (or even estimated colorimetrically) by adding a solution of lead chloride.

Scudder's indigo carmine test\(^{164}\)

In this test 4 bottles containing a 1:1 dilution of the sample with aerated tap water are incubated at 65° F (18.3° C) for 5 days. Reduced indigo carmine (prepared in a special apparatus) is used to indicate after 2, 3, 4 and 5 days whether dissolved oxygen is still present; the reduced indigo carmine turns blue if dissolved oxygen is still present but remains yellow if none is present.

\(^*\) A temperature of 27° C is now generally employed.
Methylene blue stability test
This test, involving incubation of the sample in a stoppered bottle (or a bottle provided with a water seal to exclude air) at 20°C for 5 days in the presence of 1.33 p.p.m. of methylene blue, is undoubtedly the simplest and most convenient form of incubator test. The sample is considered to have failed the test if the dye is decolorized within 5 days. The test has the advantage over the other tests mentioned above, in the case of unstable samples, of yielding information before the end of the incubation period since in such cases the colour of the dye may disappear quite early. Very grossly polluted samples decolorize the methylene blue immediately, very bad samples in 4-7 days, and bad or unsatisfactory samples in 18 hours-2 days. The presence of nitrates tends to delay the decolorization time. After the 5 days incubation period, tests may be made for sulphide (with lead acetate paper) and for nitrate (with diphenylamine reagent on a spot plate).

The test is a valuable one for determining the keeping quality of effluents and of polluted river waters. A river water failing the test within 5 days with formation of hydrogen sulphide is liable to cause odour nuisance, especially in warm weather.

Other dyes have been proposed to replace methylene blue in this test, for instance brilliant cresyl blue, but in the author’s experience, methylene blue is superior.

In the American form of the methylene blue stability test, the incubation is carried on until the dye is decolorized, or at any rate for 20 days, and the stability is then expressed as a percentage (‘relative stability number’) which is given by the equation

\[ S = 100 \left(1 - \frac{t}{20}ight) \]

where

- \( S \) = stability in per cent
- \( t \) = decolorization time in days (at 20°C)

A sample retaining its colour for 20 days is 99 per cent stable.

The American modification has the disadvantage of requiring much more incubator space than the English form of the test.

The methylene blue stability test, being dependent upon the activities of bacteria, is vitiated by the presence of germicidal substances.

AMMONIACAL NITROGEN

(‘Free and saline ammonia’) Although many methods have been suggested from time to time for the estimation of ammonia, the colormetric determination based on Luzzato’s method has shown that higher concentrations of this dye have a bactericidal action.
upon the yellow-brown coloration given by traces of ammonia and ammonium salts with Nessler’s reagent (a solution of potassium mercuri-iodide, KHgI₃, in excess of potassium hydroxide) is still the most widely used procedure. This reaction is generally referred to as ‘nesslerization’. Ammonia solutions to be nesslerized should not contain more than about 2 p.p.m. of ammoniacal nitrogen, and it is important to note that Nessler’s reagent must always be added to the ammonia solution and never vice versa, otherwise turbidity will result.

When determinations of albuminoid nitrogen or organic nitrogen are not required, a saving in time can be obtained by estimating ammoniacal nitrogen by direct nesslerization without resorting to a preliminary distillation. Many substances, however, such as calcium salts, give a cloudy solution with Nessler’s reagent. To obviate this difficulty, it is recommended in the U.S.A. that the sample be first clarified with zinc sulphate and caustic soda and that Rochelle salt (sodium potassium tartrate) be added before nesslerization. A still simpler procedure for direct nesslerization is given by Houlihan who uses a solution of sodium hexametaphosphate (‘Calgon’) to prevent development of cloudiness. (In general, however, it is more accurate to separate ammonia by distillation of the sample rendered alkaline with sodium carbonate and then determine ammonia in the distillate by nesslerization.)

Jenkins has described a new method of determining ammoniacal nitrogen involving distillation of the sample with light magnesia into a measured excess of N/140 sulphuric acid (containing a mixed methyl red–methylene blue indicator) and back-titration of the hot boiled distillate with N/140 sodium hydroxide to a green end-point. This method is said to be quicker, more precise, and more flexible than the usual procedure, and is given as a standard method in the new edition of the Ministry’s handbook.

Jenkins has shown that urea in sewage is partly recovered as ammonia during distillation with magnesia or sodium carbonate. Fresh samples of sewage containing urea should, therefore, be allowed to stand for 24 hours at room temperature (which permits hydrolysis of urea to ammonia by the urease present) before analysis for ammoniacal nitrogen unless it is desired to determine the urea content.

Organic Nitrogen and Albuminoid Nitrogen

Sewage, farm drainage, piggery wastes, vegetable processing wastes, food wastes, tannery wastes, sewage sludges, river muds, and river waters into which these wastes discharge contain varying proportions of nitrogenous organic matter. Estimations of organic nitrogen...
or of albuminoid nitrogen provide a rough index of the amount of this nitrogenous organic material present in the sample. Although it is more scientific to determine the total organic nitrogen, it has long been customary in this country to carry out the simpler estimation of albuminoid nitrogen; i.e. the proportion of the organically combined nitrogen which is converted to ammonia when the sample, after removal of ammoniacal nitrogen by distillation, is boiled and distilled with an alkaline solution of potassium permanganate under prescribed conditions. As Watson has rightly stressed, the ammonia collected in the distillate is formed by a chemical reaction and it is therefore important, in order to obtain comparable results, to standardize the amounts of sample and alkaline permanganate and the rate of the distillation.

The determination of total organic nitrogen by the well-known Kjeldahl process is, however, gradually finding favour in this country and tending to replace the albuminoid nitrogen procedure, especially in research work. For routine purposes, however, the determination of albuminoid nitrogen is quicker. Nevertheless, the time taken to perform a Kjeldahl determination can be much reduced by the adoption of semi-micro procedures.

Jenkins has described a reliable method for the routine determination of organic nitrogen involving treatment of the sample with powdered Devarda's alloy, followed by boiling for not less than 20 minutes to remove ammoniacal nitrogen and oxidized nitrogen; the organic nitrogen in the sample is then determined by Kjeldahl digestion with concentrated sulphuric acid to give ammonia, which is distilled from the alkaline solution into 1/140 sulphuric acid and nesslerized.

NITROGEN AS NITRITE (nitrous nitrogen)

Two methods are recommended by the Ministry for the quantitative estimation of nitrites:

(i) The Griess-Ilosvay method, which is based upon the diazotization of sulphanilic acid by nitrite in acid solution and the coupling of the resulting diazonium compound with alphaphethylamine to give a red azo-dye. This extremely sensitive method is satisfactory for the determination of very low concentrations of nitrite nitrogen, say less than 2 p.p.m.

(ii) The meta-phenylene diamine method, which depends upon the formation of a yellowish-brown dye by the action of nitrite in acid solution on meta-phenylene diamine. This method is suitable for the estimation of fairly high concentrations of nitrite nitrogen (2 p.p.m. or more) although it can be used for concentrations down to about 0.5 p.p.m.
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It has been shown by Klein\textsuperscript{76} that there is good agreement between results obtained by these two methods but the meta-phenylene diamine method is preferable for the higher nitrite concentrations since it avoids the preparation of very high dilutions of the sample. Sodium chloride up to about 500 p.p.m. of Cl\textsubscript{1} has little influence on the results obtained by either method but very large amounts of chloride (10,000 p.p.m. of Cl\textsubscript{1}) cause slightly high results with the Griess–Ilosvay method and rather low results with the meta-phenylene diamine method, thus making these methods unsuitable for sea-water, or for estuary water high in chloride.

Another very sensitive method for the determination of nitrite has been described by Shin\textsuperscript{90, 177}. Sulphanilamide is used instead of sulphamic acid whilst alpha-naphthylamine is replaced by the water-soluble N\textsuperscript{1}-(1-naphthyl)-ethylene diamine dihydrochloride. The sulphanilamide undergoes diazotization in hydrochloric acid by the nitrite in the sample and the diazonium compound then couples with the diamine to give a stable red azo-dye. The method is quite as sensitive as the Griess–Ilosvay method and has the further merit of giving a brighter colour, the intensity being almost independent of pH and of the amount of reagent added. The diamine is, however, much more expensive than alpha-naphthylamine. The method can be used for the determination of nitrite in estuary water or sea water as salinity has no effect upon the results\textsuperscript{178, 179}.

NITROGEN AS NITRATE (nitric nitrogen)

A rapid qualitative test for oxidized nitrogen (nitrates and/or nitrites) depends upon the intense blue coloration given with a solution of diphenylamine in concentrated sulphuric acid. The reaction is conveniently carried out on a spot plate and the intensity of the colour is a rough guide to the quantity of oxidized nitrogen present\textsuperscript{1}.

The following are the more important methods suitable for the quantitative determination of nitrate in sewage effluents and river waters:

\textit{Phenol disulphonic acid method\textsuperscript{1, 2}}

This method depends upon the reaction between phenol disulphonic acid and nitrate in sulphuric acid solution to give a nitro-derivative which develops a yellow colour when rendered alkaline with sodium hydroxide. Small amounts of chloride do not interfere but nitrite should be removed by treatment with sodium azide\textsuperscript{1}. 
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Sulphosalicylic acid method

A method similar in principle to the phenoldisulphonic acid method involves the use of a reagent containing salicylic acid; the filtered or settled sample is evaporated with a 2 per cent solution of salicylic acid in concentrated sulphuric acid, made alkaline with caustic soda, and the yellow colour matched with standards similarly treated. Advantages of this procedure are that the reagent is easily prepared and chlorides do not interfere.

Reduction to ammonia by aluminium foil in alkaline solution

The sample is evaporated with a little sodium carbonate to remove ammonia and the oxidized nitrogen is reduced to ammonia by aluminium foil in a solution made alkaline with sodium hydroxide. After standing overnight, the ammonia formed is estimated in an aliquot by nesslerization. This gives the total oxidized nitrogen from which nitrate nitrogen is calculated by deducting the nitrite nitrogen figure.

Reduction to ammonia by zinc–copper couple in acetic acid solution

The sample, after removal of ammonia, is reduced to ammonia with zinc–copper couple in dilute acetic acid solution and the ammonia produced is distilled and estimated in the distillate by nesslerization.

When the sample has a relatively high nitrite content, a preliminary treatment with acetic acid solutions of alpha-naphthylamine and sulphanilic acid is necessary to remove nitrite.

Devarda's alloy method

Jenkins uses the residual liquid remaining in the distillation flask after ammoniacal nitrogen has been determined by distillation with magnesia (page 283) and treats it with Devarda’s alloy to reduce oxidized nitrogen to ammonia. The ammonia produced is then estimated by distillation into excess of $\text{H}_2\text{SO}_4$ sulphuric acid followed either by back-titration with $\text{Na}_2\text{CO}_3$ sodium hydroxide, or, if the oxidized nitrogen is low (less than 4 p.p.m.) by nesslerization.

Rapid method using brucine

This useful method, based upon an old procedure described by Haase, is suitable as a rapid field test for the approximate estimation of nitrate in river water. A disc covering the range 1–9 p.p.m. of nitrate nitrogen has been prepared for this purpose by the Tintometer Ltd. for use with the Lovibond comparator. The sample (1 ml.) is treated with 0.1 ml. of a 5 per cent solution of brucine in glacial acetic acid, then with 2 ml. of pure nitrogen-free sulphuric acid and the mixture is shaken and allowed to stand for
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7 minutes. The yellow colour is matched against the colour standards of the Lovibond disc, using as a blank 1 ml of distilled water plus the reagents in the left-hand compartment of the comparator. Chloride up to 1000 p.p.m. does not interfere but larger amounts should be removed with silver sulphate. Nitrite, if present, must be separately estimated and an appropriate correction applied.

SULPHIDE

Sulphides are present in septic sewage, ammoniacal gas liquor, tannery wastes, sulphide dye liquors, viscose rayon wastes, oil refinery wastes, and in drainage from many tips. They may also occur in samples containing proteins which have been stored and have undergone anaerobic decomposition.

The accurate determination of small amounts of sulphide is a difficult matter in the author's opinion, and none of the published methods are entirely satisfactory or applicable to all types of samples. The determination is complicated by the property of hydrogen sulphide and other sulphides of undergoing oxidation to sulphur in the presence of air or oxygen. The presence of sulphides is usually shown by their characteristic odour of rotten eggs but this may not be apparent with insoluble sulphides or with strongly alkaline solutions of soluble sulphides.

The detection of sulphide is comparatively easy and can be carried out by putting the sample in a 100 ml glass-stoppered conical flask, acidifying and suspending between the stopper and neck a slightly moistened lead acetate paper. A brown stain on the paper indicates the presence of sulphide; using a 50 ml sample, as little as 0.01 p.p.m. of \( \text{H}_2\text{S} \) can be detected in this way. Another sensitive test for sulphides, detecting 0.1 p.p.m. or even less, is based on Raschig's azide-iodine reaction which was first utilized as a spot test for sulphides by FEUZ.

The test is particularly useful for testing a series of samples in river survey work and is carried out by MUELLER and RAND as follows: The sample (1 ml) is placed on a watch glass over black paper, 1 ml of 30 per cent sodium azide is added followed by 1 ml of \( \text{N}/10 \) iodine solution. In the presence of sulphide, bubbles of nitrogen develop on the surface of the glass within 2-5 minutes. The formation of these bubbles depends upon the fact that the reaction between sodium azide and iodine to give nitrogen gas, which is normally extremely slow, is catalytically accelerated by traces of soluble or insoluble sulphides:

\[
2\text{Na}\text{N}_3 + \text{I}_2 \xrightarrow{\text{catalysed by sulphide}} 2\text{NaI} + 3\text{N}_2
\]

The only interfering sulphur compounds are thiosulphates and thiocyanates which also catalyse the azide-iodine reaction.
The best and most sensitive colorimetric method for estimating sulphide is based upon the fact that hydrogen sulphide and sulphides in the presence of sufficient hydrochloric acid and an oxidizing agent (ferric chloride) react with p-aminodimethylaniline hydrochloride (p-dimethyl-p-phenylene diamine hydrochloride) to produce the dye methylene blue in accordance with the equation:

\[
\begin{align*}
2\text{C}_6\text{H}_4 + 6\text{FeCl}_3 + \text{H}_2\text{S} &\rightarrow \text{N} \quad \text{S} + 6\text{FeCl}_2 + 6\text{HCl} + \text{NH}_4\text{Cl} \\
\text{NH}_4\text{Cl} &\rightarrow \text{C}_6\text{H}_5 \\
\text{N(CH}_3)_2 &\rightarrow \text{Cl}
\end{align*}
\]

Details of the quantitative method as applied to sewage were first worked out by Pomeroy\(^1\) and the method is now a standard one in the U.S.A.\(^2\). It will determine sulphide in concentrations of 0.1–20 p.p.m. of H\(_2\)S and, by the use of larger volumes, concentrations as low as 0.01 p.p.m. can be estimated. Dissolved sulphide as well as sulphide bound as insoluble iron, zinc, manganese, and lead sulphides, can be determined, but copper sulphide is too insoluble to react. It is possible to estimate sulphides in sludges and river muds by this method\(^1\). Concentrations of sulphite and thiosulphate above 10 p.p.m. cause some interference but, according to Pomeroy, by increasing the amount of ferric chloride and lengthening the reaction time, up to 50 p.p.m. of these compounds can be tolerated.

Another method for determining total sulphide is based upon the volatilization of hydrogen sulphide from an acidified solution of the sample by a stream of inert gas (nitrogen or carbon dioxide\(^*\)), the evolved hydrogen sulphide being absorbed in a solution of zinc acetate. The zinc sulphide produced is then determined by an iodometric titration procedure\(^1\)–\(^2\). The method is accurate in the absence of sulphite and thiosulphate which may cause serious errors due to interaction of H\(_2\)S and SO\(_2\) on acidification giving free sulphur. The method is, however, tedious and time-consuming, and is unsuitable for routine work since in view of the extensive

\(^*\) These gases must be freed from oxygen.
apparatus required only one determination at a time can conveniently be carried out.

A simple routine iodometric method for determining total sulphide in certain trade effluents containing sulphite and thiosulphate has been described by Pomeroy and used for the estimation of sulphide in petroleum waste waters. The sulphide is precipitated by adding zinc acetate and sodium carbonate to the sample. After settling, the non-sulphide iodine demand is determined on one-half of the supernatant liquid (thus giving the non-sulphide iodine demand of half the sample) and the iodine demand (due to sulphide and one-half of the non-sulphide) is then determined on the remainder (thus giving the sulphide iodine demand plus the non-sulphide demand of half the sample). The method is suitable for sulphide in the range 0.2–100 p.p.m. It does not, however, give accurate results with sewage and other samples containing much colloidal and suspended organic matter since any organic matter associated with the zinc sulphide precipitate causes some interference by reacting with iodine.

A useful routine method of estimating sulphides in river waters has been developed by Houlihan and Farina, and is based upon the application of the Winkler technique used for the determination of dissolved oxygen. Manganese chloride reagent is added to the sample (500 ml.), followed by the alkaline iodide azide reagent, and after settling the precipitate, N/80 iodine* is added and the mixture is acidified and then titrated with N/80 sodium thiosulphate. Absorption of iodine is due to sulphides and any other substances which react with iodine. A correction for any non-sulphide iodine demand is made by carrying out a blank determination on a portion of the sample freed from sulphide by passing oxygen-free nitrogen through the acidified solution. Simple apparatus for performing the test is described in the original paper.

An approximate method used in the past for estimating sulphides in trade wastes involved determinations of the iodine consumption of the sample before and after expelling all the hydrogen sulphide by boiling. Although rapid and suitable for routine work, the method is open to several objections. For instance, there may be loss of volatile iodine-consuming compounds other than hydrogen sulphide (e.g. phenols) which would cause high results. Again, acidification would be necessary to expel all the sulphide from insoluble sulphides, but in the presence of thiosulphate (which is often associated with sulphide) there would be an error due to interaction of H₂S and SO₂.

The methods for sulphide so far outlined give total sulphide, i.e.

* N/80 potassium permanganate can also be used since it liberates an equivalent of iodine from the iodide when acid is afterwards added.
dissolved sulphide plus insoluble sulphide. If dissolved sulphide only is required, the suspended matter is removed by filtration in a current of pure nitrogen and $\text{H}_2\text{S}$ is liberated from the filtrate by acidification and absorption in zinc acetate solution; an apparatus for performing this determination is described by Wheatland and Lowden.\textsuperscript{186A}

**SULPHITE**\textsuperscript{18A}

Sulphite is present in waste waters from paper works using bisulphites in the preparation of cellulose from wood pulp, in certain wastes from the manufacture of cellophane, and in river waters receiving these wastes.

In the absence of thiosulphate, sulphite can be detected by heating the sample, acidified with sulphuric acid, when sulphur dioxide is evolved which is identified by the blue coloration produced when a piece of filter paper moistened with a mixture of potassium iodate solution and starch solution is held in the vapours:

$$2\text{KIO}_3 + 5\text{SO}_2 + 4\text{H}_2\text{O} = \text{I}_2 + 2\text{KHSO}_4 + 3\text{H}_2\text{SO}_4$$

Another sensitive test for sulphites\textsuperscript{94} is based upon the fact that in neutral solution they decolorize dilute solutions of triphenylmethane dyestuffs. The sample, neutralized with sodium bicarbonate if necessary, is treated with an equal volume of a dilute solution of malachite green (2-5 mg per 100 ml.) when the green colour is immediately bleached if sulphite is present. Thiosulphates do not interfere.

Sulphite can be estimated by adding the sample to a known excess of iodine solution and determining the unused iodine by titration with standard sodium thiosulphate. This is only an approximate method since organic matter, thiosulphate and sulphide all cause interference. A modification of this method is used by Kohout\textsuperscript{187} for the determination of the ‘iodine numbers’ of river waters in order to detect the presence of wastes from sulphite cellulose factories. The river water (100 ml.) is placed in a graduated cylinder and distilled water (100 ml.) in a similar cylinder. Starch and potassium bicarbonate are added to each cylinder and 0.01N iodine solution is run in until the blue colours are identical in each cylinder. The results are expressed as iodine numbers in p.p.m.

Uncontaminated river waters give iodine numbers of 2-6, whilst waters contaminated by sulphite cellulose wastes yield numbers
varying from 19–202. Other substances present (e.g. phenols, urea) are usually not present in amounts sufficient to cause any appreciable interference with the test.

**SULPHATE**

The determination of sulphate is rarely called for except in connection with problems involving the corrosion of concrete (cf. page 35).

The standard procedure for estimating sulphate involves the addition of barium chloride to the sample acidified with hydrochloric acid and the gravimetric determination of the precipitated barium sulphate.\(^2\) The method, which requires strict attention to detail, is fairly accurate but is tedious and unsuitable for very small amounts of sulphate.

The evaluation of the barium sulphate precipitate can also be carried out, according to Belcher, Gibbons and West, by dissolving it in excess of a boiling ammoniacal solution of 0.02M ethylene diamine tetra-acetic acid (EDTA) and back-titrating with standard magnesium chloride using Solochrome Black as indicator.

A volumetric method first described by Schroeder utilizes an internal indicator (tetrahydroxyquinone) to detect the end-point in the reaction between sulphate and barium chloride; the first slight excess of barium chloride causes a colour change from yellow to red but unfortunately the end-point is not particularly sharp.

The best volumetric method for the estimation of sulphate is based upon the precipitation of sparingly soluble benzidine sulphate followed by the titration of the washed precipitate with standard sodium hydroxide using phenolphthalein as indicator.\(^2\) The use of a modification of this method described by McConnell and Ingols permits the determination of sulphate in the range 2–400 p.p.m. of \(\text{SO}_4\). There is interference by phosphate.

A rapid method specially suitable for the estimation of low sulphate concentrations depends upon the turbidity produced when barium chloride is added to a sample containing traces of sulphate. The conditions for this determination must be rigidly standardized. In a recent modification in which the turbidity produced by barium sulphate is measured spectrophotometrically in 1 cm cells at a wavelength of 380 m\(\mu\), sulphate can be determined in 10 minutes over the range 2–80 p.p.m. of \(\text{SO}_4\). Interference by phosphate or carbonate is prevented by carrying out the reaction in dilute hydrochloric acid solution.
The carbon dioxide over and above that required to convert alkali
or alkaline earth carbonates to bicarbonates is generally called
‘free carbon dioxide’. It accelerates corrosion and is toxic towards
fish.

A special sample of the water in a completely filled bottle should
be taken for this estimation. The usual method of determination
is only an approximate one and involves titration of the sample
of water in a Nessler tube with standard sodium hydroxide or
sodium carbonate in the presence of phenolphthalein until the
indicator acquires a faint permanent tint. If the sample is acid
towards methyl orange (pH below 4·0), the mineral acidity must
be determined and a correction applied. Corrections should also
be applied if iron and aluminium salts are present.

An accurate but rather lengthy method for determining free
carbon dioxide is given by Parkhouse. It involves the transfer-
ence of the carbon dioxide by means of a current of carbon dioxide-
free air to a solution of sodium hydroxide and the titration of the
resulting mixture of sodium hydroxide and sodium carbonate with
standard hydrochloric acid to phenolphthalein and to the B.D.H.
‘4·5’ indicator. The method is capable of determining up to 10
p.p.m. of carbon dioxide with an accuracy of 0·1 p.p.m.

If the pH value and the methyl orange alkalinity of a sample are
both known, it is possible, according to Kozma, to calculate the
free carbon dioxide approximately by means of the following equa-
tion:

\[
\log \text{CO}_2 = \log \text{alkalinity} + 6·3075 - \text{pH}
\]

where \(\text{CO}_2\) = free carbon dioxide in p.p.m.
and alkalinity = methyl orange alkalinity (expressed as p.p.m. of
\(\text{CaCO}_3\)).

\[\text{FREE CHLORINE}\]

In problems connected with river pollution, ‘free chlorine’ is
generally taken to mean chlorine present as molecular chlorine
(\(\text{Cl}_2\)), hypochlorous acid (\(\text{HClO}\)), or hypochlorites (e.g. \(\text{NaClO}\),
chloramines (\(\text{NH}_2\text{Cl}, \text{NHCl}_2, \text{NCl}_3\)) or similar compounds cap-
able of yielding available chlorine (e.g. organic chloramino com-
pounds); all of these can liberate iodine from potassium iodide in
acid solution and can give a yellow coloration when treated with
an acid solution of e-tolidine. These reactions form the basis of
methods for the quantitative determination of free chlorine.

In dealing with potable waters, however, it is customary to make
a distinction between ‘free available chlorine’ (e.g. chlorine present
as molecular chlorine, hypochlorous acid, or hypochlorite*) and 'combined available chlorine' (e.g. chlorine combined with ammonia in the form of chloramines or other nitrogenous compounds †) and methods are in use (e.g. the o-tolidine-arsenite test) for distinguishing between these various forms. The reason for this distinction lies in the fact that, in the case of drinking waters, we are more concerned with the destruction of bacteria, and the bactericidal action of chloramines is considerably slower than that of molecular chlorine or hypochlorites. Since there appears to be little difference in toxicity to fish between 'free available chlorine' and 'combined available chlorine', there is little point in differentiating between these forms of chlorine in river pollution work. However, part of the well-known o-tolidine-arsenite test allows compensation for interfering substances (such as nitrates and the oxidized forms of iron and manganese) and it is, therefore, recommended that when these interfering substances are present, the use of sodium arsenite be adopted. If sodium arsenite be added before the o-tolidine, it prevents colour formation by chlorine and chloramines, but does not inhibit colours due to interfering substances. This reading can then be deducted from that given by the direct o-tolidine test.

Neither the potassium iodide test nor the o-tolidine test is specific for free chlorine. Nitrates, ferric salts, manganic compounds and many other oxidizing agents give a yellow coloration with o-tolidine in acid solution but, as already mentioned, their interference can be circumvented by the use of sodium arsenite. A large number of oxidizing agents, besides free chlorine (e.g. nitrates, ferric salts chromates), liberate iodine from an acid solution of potassium iodide.

Milton197 has described a test for free chlorine which is not only twice as sensitive as the o-tolidine test but is almost specific since only free bromine reacts similarly. The sample (5 ml.) is treated with 1 ml. of 1 per cent aqueous sodium cyanide and then with 5 ml. of a 25 per cent aqueous solution of pyridine containing 2 per cent of benzidine hydrochloride. A reddish colour develops, reaching its maximum within 10 minutes. This test has been modified by Morris and Grant198 to permit the determination of total available chlorine in water.

Belcher, Nutten and Stephen199 have reported that 3:3'-dimethylaminophthidine (0·1 per cent solution in glacial acetic acid) is superior to o-tolidine as a reagent for chlorine in sensitivity and in

*) The relative proportions of Cl₂, HClO, or hypochlorite depend on the pH value.
† The type of chloramine present depends on the Cl₂:N ratio and on the pH value.
the stability of the colour produced. It is about ten times as sensitive as o-tolidine and gives a stable red colour which is suitable for the photometric determination of free chlorine in the range 0·05-1·0 p.p.m. Other oxidizing agents interfere.

Chlorides are present in sewage, sewage effluents and farm drainage, and in large amounts in certain acid pickle liquors (as free hydrochloric acid), in brine from a salt works, in spent regenerant solution from water softening plants using the base-exchange process, in oil-well waters, and in tidal waters containing sea water. In estuarial waters, it is necessary to determine the chloride content not only to calculate the proportion of sea water present (see page 375) but also to compute the percentage saturation of dissolved oxygen.

The usual method of determining chloride in river waters is the volumetric procedure originally put forward by Mohr. This depends upon the precipitation of silver chloride by addition of a dilute standard solution of silver nitrate (1 ml. = 1 mg of Cl) in the presence of potassium chromate indicator, which, just after the end-point is reached, forms a reddish precipitate of silver chromate with the slightest excess of silver nitrate, so that the colour changes from the yellow due to potassium chromate to a faint orange-red. Common interfering substances are acids, alkalis, sulphides, thiocyanates, phosphates, cyanides, sulphites and any anions forming sparingly soluble silver salts. Acidity should be neutralized by addition of a little pure chloride-free sodium bicarbonate or calcium carbonate. If the sample is appreciably alkaline towards phenolphthalein or contains sulphide, the addition of a few crystals of zinc sulphate will prevent interference. Thiocyanate, if present, can be separately estimated and a correction made to the titration; alternatively, thiocyanate can be destroyed by boiling with hydrogen peroxide. Sulphites can be rendered harmless by addition of hydrogen peroxide. Coloured samples can often be decolorized by flocculation with zinc sulphate and sodium carbonate.

The Mohr titration method is suitable for river waters and effluents containing about 5-200 p.p.m. of Cl. With higher concentrations of chloride, a suitable dilution should be used.

A simple colorimetric method for chloride has been described based upon the reddish-brown colour obtained by adding to 100 ml. of the water sample 1 ml. of 10 per cent potassium chromate and 0·45 ml. of N/55·5 silver nitrate. The colour is compared after 1 minute with standards within the range 0·4-2·0 p.p.m. of Cl.

* The chloride equivalent can be calculated from the relation $S \times 1·11 = \text{Cl}$
The method is accurate to about 2 per cent. Acid or alkaline waters should be neutralized and preliminary treatment is necessary in the presence of iron, sulphide, or much organic matter.

Although mercurimetric methods for the volumetric determination of chloride depending on the formation of slightly dissociated mercuric chloride are quite old, they have not until recently achieved much popularity. A tentative procedure, somewhat more sensitive than the Mohr method, is now given in the latest edition of the A.P.H.A. Standard Methods and involves addition of standard mercuric nitrate to the sample adjusted to pH 3·1 and containing a mixed indicator (diphenylcarbazone + bromophenol blue) which turns violet at the end-point.

**Fluorides**

Fluorides occur in certain chemical waste waters (e.g. effluents from the production of aluminium from bauxite and from the manufacture of phosphatic fertilizers), in some waters from oil wells, in effluents from atomic energy plants, and in waste waters from the scrubbing of flue gases and from the etching of glass.

Volumetric methods for the determination of fluoride are generally based upon the titration of the sample with standard thorium nitrate in a solution buffered at about 2·9–3·3, using sodium alizarin sulphonate as indicator; the colour at the end-point changes to pink due to the formation of a lake between the alizarin and the slightest excess of thorium ions. The method as applied to natural waters is described by Bond and Murray, the titration being carried out at pH 3·3 in the presence of acetic acid; a preliminary treatment with barium chloride eliminates interference of sulphate, phosphate and carbonate. Interference of aluminium occurs. Milton has found that the use of the sodium salt of sulphotrichlorhydrindimethyI-fuchsin dicarboxylic acid (Solochrome Brilliant Blue BS or Chrome Azulol S) as indicator in place of sodium alizarin sulphonate gives a much sharper end-point in the titration.

The most popular method of estimating low concentrations of fluoride in waters is the colorimetric procedure based on the Scott modification of the Sanchis method and depends upon the bleaching action of fluorides on the reddish lake formed by zirconium oxychloride or nitrate and sodium alizarin sulphonate in hydrochloric acid and sulphuric acid solution. Any interference due to free chlorine can be prevented by adding to 100 ml. of the sample 1 drop of N/10 sodium thiosulphate for each 1·8 p.p.m. of chlorine. If more than 500 p.p.m. of Cl, 200 p.p.m. of SO₄²⁻, 200 p.p.m. (expressed as CaCO₃) of acidity or alkalinity, 2 p.p.m.
of Fe, 0.5 p.p.m. of Al, or 1 p.p.m. of PO$_4^{3-}$ are present, interference occurs and it is preferable to separate the fluoride by a distillation procedure (e.g. steam distillation with perchloric acid or concentrated sulphuric acid in the presence of glass beads) to volatilize the fluoride as silicon tetrafluoride. Factors affecting this distillation are discussed by Megrelian and Solet.

Lamar has shown that if the zirconium salt–alizarin reagent is made up with 2N sulphuric acid instead of with a mixture of hydrochloric and sulphuric acids, much more sulphate and chloride can be tolerated without any interference, namely up to about 500 p.p.m. of SO$_4^{2-}$ and about 1,000 p.p.m. of Cl. Megrelian and Maier have described an improved method suitable for the spectrophotometric and visual determination of fluoride in waters, using a reagent with zirconium–alizarin ratios different from those used in the other methods. The visual method, which uses a reagent prepared, as suggested by Lamar, with sulphuric acid instead of mixed hydrochloric and sulphuric acids, covers the range 0–2 p.p.m. of F and is sensitive to increments of 0.02 p.p.m. of F. This procedure appears to be more reliable than the other methods and gives better colours for matching.

A fluorometric method for traces of fluoride (as little as 0.2 gamma of F) has been described by Willard and Horton and is based on the decrease caused by fluoride in the fluorescence of an aluminium–morin complex in 50 per cent alcoholic solution at pH 4.9.

**Hardness**

The total hardness, or soap-consuming power, of a water is generally regarded as the sum of the concentrations of the calcium and magnesium ions but can also include all other metallic ions reacting with soap (e.g. Fe, Al, Zn, Mn, Sr) with the exception of the alkali metal ions. Although the most accurate method of arriving at a hardness figure is to add together the concentrations of calcium, magnesium, and other metals causing hardness, this is rather tedious and in practice quicker routine methods have been used. These include the Clark and Wanklyn soap titration tests (which depend upon the formation at the end-point of a permanent lather), the Blacher potassium palmitate procedure, and the Wartha–Pfeifer method (involving boiling with caustic soda–sodium carbonate and titrating the clear filtrate or supernatant liquid with N/10 acid). All these methods have now been rendered virtually obsolete by the elegant and rapid ‘versenate’ titration method of Schwarzenbach and his co-workers. According to this procedure, the calcium and magnesium ions are titrated in a buffered solution with a standard solution of disodium ethylene diamine tetra-acetate
DETECTION AND MEASUREMENT

(EDTA or 'sodium versenate') in the presence of an alcoholic solution of a blue dye, Eriochrome Black T*; this indicator forms red unionized complexes with calcium and magnesium at a pH value of about 10, and as soon as these ions have been sequestered by the titrant there is a colour change from red to blue which marks the end-point. There is now a very extensive literature on this method. Diskant claims that diethanolamine and triethanolamine are superior to ethyl alcohol for preparing stable indicator solutions. Bate and Nois state that if sodium sulphide is incorporated in the titrant, the following ions do not interfere: 10 p.p.m. of copper, zinc, lead, tin and aluminium; 20 p.p.m. of ferrous or ferric iron; 10,000 p.p.m. of SO_4^{2-} or Cl^-; 500 p.p.m. of SO_4^{2-}, CrO_4^{2-}, NO_2^- or NO_3^-; 1,000 p.p.m. of CO_3^{2-}; and 200 p.p.m. of SiO_2.

Schwarzenbach also showed that calcium ions alone can be determined if murexide (ammonium purpurate) is used as indicator. In a modification of this procedure proposed by Knight, the colour change at the end-point is rendered more easily visible by incorporating Naphthol Green B with the murexide, the change of colour then being from olive-green through grey to blue.

The classical volumetric method of determining calcium ions involves precipitation of calcium as the oxalate, solution of the washed precipitate in hot dilute sulphuric acid, and titration at 70–80°C with N/10 or N/100 potassium permanganate. If appreciable organic matter is present, it should first be destroyed by evaporation with nitric acid. The separation of calcium from many interfering ions (e.g. silicate, phosphate, iron, aluminium, manganese, titanium, and magnesium) can be achieved by precipitating the calcium as oxalate from a solution containing such organic acids as oxalic acid or acetic acid at a pH value of about 4. In the procedure of Lingane, the hydrochloric acid solution containing calcium and any interfering ions is heated almost to boiling, treated with hot ammonium oxalate solution, and the calcium oxalate is precipitated by adding ammonia drop by drop with stirring until the pH rises to 4.0 ± 0.5; it is convenient to use methyl orange as indicator and a potassium hydrogen phthalate buffer for comparison.

Hardness is usually expressed in this country in terms of calcium carbonate, the unit being 1 p.p.m. of CaCO_3. Conversion to and from other units can be carried out with the aid of Table 110 in the Appendix.

* This is the sodium salt of 1-(1-hydroxy-2-naphthylazo)-5-nitro-2-naphthal-4-sulphonic acid (No. 203 in the Colour Index of the Society of Dyers and Colourists).
One of the outstanding advances made in analytical chemistry within recent years is the increasing use of organic reagents for the detection and estimation of traces of metals. Such compounds as dithizone, o-phenanthroline, sodium diethyldithiocarbamate, and diphenylcarbazide—at one time chemical curiosities—are now comparatively common reagents in most well-equipped laboratories. Many of these reagents are almost specific for a particular element, or at any rate highly selective, and some are sensitive enough to permit the determination of concentrations of metal as low as 0·01–0·1 p.p.m. Examples of some organic reagents suitable for the colorimetric determination of traces of the commoner metals are given in Table 56.

Table 56: Some organic reagents suitable for the colorimetric estimation of traces of the commoner metals

<table>
<thead>
<tr>
<th>Metal</th>
<th>Organic reagent</th>
<th>Colour produced</th>
<th>Approximate pH</th>
<th>Maximum concentration of metal (mg/l)</th>
<th>Useful range for visual estimate of p.p.m. of metal</th>
<th>References (etc.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cadmium</td>
<td>Dithizone</td>
<td>red</td>
<td>strongly alkaline solution</td>
<td>510 (a)</td>
<td>1, 91, 92</td>
<td></td>
</tr>
<tr>
<td>Chromium</td>
<td>Diphenylcarbazide</td>
<td>red</td>
<td>acid solution</td>
<td>540 (a)</td>
<td>1, 90, 91</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Dithizone</td>
<td>violet</td>
<td>0·04–2·0</td>
<td>1, 90, 91, 92, 233</td>
<td>1, 90, 91, 92, 233</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Na dithizone</td>
<td>yellow</td>
<td>0·04–2·0</td>
<td>1, 90, 91, 92, 233</td>
<td>1, 90, 91, 92, 233</td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>Cupricine (2:2' bromophenol)</td>
<td>purple</td>
<td>2·0</td>
<td>545 (a)</td>
<td>220</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Thioglycollic acid</td>
<td>red</td>
<td>0·01–2·0</td>
<td>508 (a)</td>
<td>91, 92</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Tripyridyl</td>
<td>purple</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Iron</td>
<td>Dithizone</td>
<td>red</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td>Dithizone</td>
<td>red</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td>Dithizone</td>
<td>red</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td>Dimethylglyoxime</td>
<td>red</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Uranium</td>
<td>Dibenzoylmethane</td>
<td>red</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>Dithizone</td>
<td>blue</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>Zincon</td>
<td>blue</td>
<td>0·01–2·0</td>
<td>9·6 (a)</td>
<td>1, 90, 91, 92, 98</td>
<td></td>
</tr>
</tbody>
</table>

(a) = 30 ml. Nessler tubes. (b) = 100 ml. Nessler tubes.

* Using 5 ml. or 10 ml. of sample and extracting with 5 ml. of 0·001 per cent dithizone in CCl₄.
One of the most versatile and useful of these reagents is dithizone (or, diphencylthiocarbazone)$^{91, 92}$, which by replacement of one or both hydrogen atoms forms highly coloured dithizonates with no less than seventeen of the metals (manganese, iron, cobalt, nickel, copper, zinc, lead, silver, cadmium, indium, platinum, palladium, tin, mercury, thallium, bismuth and gold). The dithizone is used as a dilute (0.001 per cent) solution in chloroform or carbon tetrachloride (which is green) and the aqueous sample is extracted with this reagent when the colour of the organic solvent changes from green to that of the metal dithizonate (red, purple, yellow, etc., depending upon the particular metal). In order to make this reagent specific for a particular metal, various devices can be employed, such as adjustment of pH, or use of cyanide, thiosulphate and thiocyanate as complex-forming agents. Thus, in slightly alkaline solution containing cyanide, only lead, thallium, stannous tin and bismuth react to form dithizonates. Bismuth can be extracted from a slightly acid solution and so can be separated from lead. Tin does not react with dithizone if oxidized to the stannic form. In dilute mineral acid solution, only palladium, gold, silver, mercury and copper react with dithizone (also bismuth incompletely).

In view of the extreme toxicity of many metals towards fish (see Chapter 7), other animal life, vegetable life and bacteria, the importance of reliable methods for the determination of traces of these metals in river waters, sewage effluents, and trade effluents needs little justification. Practical details of the methods used are given in the invaluable reference books by Allport$^{90}$, Sandell$^{91}$ and Snell and Snell$^{92}$, in various handbooks of standard methods$^{1, 2, 3}$, in papers by Riehl$^{219}$, Butts and his associates$^{220, 221}$, and in a valuable series of monographs recently published by Hopkin and Williams$^{222}$.

It is advisable, before proceeding to the quantitative determination of the metal or metals, to carry out a preliminary qualitative examination of the sample, for if certain interfering elements can be shown to be absent the quantitative procedure can often be much simplified and valuable time saved. Spot tests, using drops of sample and reagents on white porcelain spot plates or on filter paper are particularly useful in this connection and are given in Fegly's book$^{24}$, in a paper by Butts and his associates$^{219}$, and in a report of an international committee$^{28}$.
It is of the greatest importance that reagents and distilled water used for the detection and estimation of traces of metals should be as free as possible from metallic contamination. Distilled water should not be prepared in a copper still in order to avoid contamination with copper. Special reagents virtually free from arsenic and lead can be purchased. In all cases of doubt, it is essential that blank determinations should be carried through all the stages of the particular method, thus enabling the result of the sample analysis to be corrected, but naturally the accuracy of the sample determination is much reduced if the blank value obtained with the reagents and distilled water is unnecessarily large.

**Arsenic**

Arsenic is found in many weed-killers, in some sheep-dipping liquors and in some tannery effluents.

A very sensitive qualitative test for arsenic in waters, based on the Reimisch reaction, is described by Sacchetta and Machado. The water (25 ml.) is evaporated to dryness, the residue taken up in water (1 ml.), concentrated hydrochloric acid (1 ml.) is added, and a copper wire is inserted. After heating on the water bath for 15 minutes, a grey coloration due to As$_2$Cu appears on the wire if more than 0.2 p.p.m. of arsenic is present in the sample.

The most popular method of estimating traces of arsenic in waters is based upon the well-known Gutzzeit test. The arsenic, obtained by wet digestion of the sample with sulphuric and nitric acids and reduced to the trivalent state by a suitable reducing agent (e.g., sodium sulphite), is volatilized as arsine (AsH$_3$) with arsenic-free zinc and hydrochloric acid in the presence of stannous chloride, and the evolved gas, after passing through glass wool containing lead acetate to absorb any H$_2$S, is allowed to react with paper impregnated with mercuric chloride or bromide. The yellowish-brown stain so produced is compared with a series of stains given by standards ranging from 0.001–0.05 mg of arsenic.

**Barium**

Barium may occur in effluents from places where barytes (BaSO$_4$), witherite (BaCO$_3$) and other barium minerals are mined. Soluble barium compounds are poisonous.

There is a scarcity of good procedures for the determination of small amounts of barium and the only available chemical methods are the colorimetric estimation as barium chromate and the more sensitive turbidimetric estimation as barium sulphate. If barium is present as insoluble barium sulphate, it can be brought into solution by fusing with sodium carbonate, leaching the
melt with water, and dissolving the well-washed residue of barium carbonate in dilute hydrochloric acid.

A sensitive method of detecting and determining barium is by spectrum analysis (page 267). According to WILSKA, the smallest concentration of barium that can be determined in this way is 0.05 p.p.m.

**Cadmium**

Cadmium occurs in cadmium plating effluents, and its compounds are poisonous.

It can easily be detected in small amounts (about 1 p.p.m.) by the intense red precipitate formed when a drop of the filtered ammoniacal sample is treated on filter paper with a saturated solution of ferrous-2,2'-dipyridyl complex containing excess of potassium iodide. Before the advent of dithizone, cadmium was determined colorimetrically in ammoniacal cyanide solution as the yellow colloidal sulphide. Small amounts of zinc, nickel, cobalt and copper do not interfere, but iron and lead interference occurs and these metals must be removed.

SERFASS and his associates determine cadmium colorimetrically with dithizone in effluents containing organic matter and most common ions. The organic matter is first destroyed by wet digestion of the sample with nitric and sulphuric acids. Any silver, mercury, and copper present are then removed by extraction with dithizone in mineral acid solution. Nickel and cobalt are complexed with dimethylglyoxime; the nickel complex is extracted with chloroform whilst the cobalt complex, though not extracted by chloroform, does not react with dithizone. Cadmium is then estimated colorimetrically by means of the red complex it forms with dithizone in strongly alkaline solution. BUTTS and his co-workers adopt a different procedure for dealing with interfering elements before determining cadmium with dithizone.

**Chromium**

Chromium may occur as hexavalent chromium (chromate or bichromate) in waste waters from the manufacture of chromates, in chromium plating wastes, in wastes from the anodizing of aluminium, and as trivalent chromium in chrome tanning liquors. Chromates are yellow, bichromates are orange and trivalent chromium salts are generally green. Chromates are poisonous and strongly bactericidal.

A very sensitive qualitative test for hexavalent chromium depends upon the intense violet coloration obtained on the addition of a
solution of d-diphenylcarbazide,

\[
\text{CO} \quad \text{NH-NH-C}_6\text{H}_5
\]

in alcohol, acetone or acetic acid to an aqueous solution of a chromate acidified with sulphuric acid, hydrochloric acid or acetic acid. According to Sandell 91, the optimum acidity for this test is about 0.2N and the best acid to use is sulphuric acid. The test is nearly specific, only mercury and molybdenum reacting in a similar way in acid solution. The yellow coloration given by ferric iron can be prevented by addition of phosphoric acid. Solutions of diphenylcarbazide are not very stable, but, according to Ede and Silverman 228, a reagent stable for 5 months can be prepared by incorporating phthalic anhydride in the alcoholic solution. Trivalent chromium gives no colour with diphenylcarbazide and must, therefore, be first oxidized to the hexavalent form either with sodium peroxide or by boiling the acid solution (containing a little silver nitrate as catalyst) with potassium persulphate. Although the estimation of not too small amounts of hexavalent chromium can be carried out colorimetrically by taking advantage of the intense yellow colour of chromates in alkaline solution, a more sensitive and reliable method, which can be carried out directly on the centrifuged sample, is based on the use of diphenylcarbazide in acid solution. In the method given by Sorous 229 for the estimation of total chromium (trivalent + hexavalent) in sewage, the sample is treated with sodium sulphite and concentrated sulphuric acid to reduce any chromate to the trivalent condition. This preliminary reduction is necessary to avoid any subsequent loss of chromium as volatile chromyl chloride. After digesting to destroy organic matter, potassium permanganate is added to oxidize trivalent chromium to hexavalent chromium, any excess of permanganate being subsequently destroyed by adding a few drops of concentrated hydrochloric acid. The chromate is then estimated with diphenylcarbazide.

When chromates are present in fair quantity, one of the following volumetric methods can be used for the quantitative determination:

(a) Titration of the solution acidified with sulphuric and phosphoric acids with standard ferrous ammonium sulphate using diphenylamine or diphenylamine sulphanic acid as indicator 84, 85.

(b) The acidified sample is treated with potassium iodide and the liberated iodine estimated with standard sodium thiosulphate using starch as indicator. Nitrites, if present, interfere with
Copper occurs in copper pickling liquors, copper plating wastes, and cuprammonium rayon wastes. Copper compounds are very toxic to fish and other animal life in streams and are extremely toxic to algae and other vegetable life and to bacteria.

Traces of copper can be detected by shaking the sample, slightly acidified with mineral acid, with a very dilute (0.001 per cent) solution of dithizone in carbon tetrachloride. In the presence of copper, the green colour of the reagent changes to violet-red. The test is not affected by the presence of cyanide and the only common interfering elements are mercury and silver. Another very sensitive test for small amounts of copper is based on the yellow or brown coloration (or precipitate) given by ammoniacal solutions of cupric salts with sodium diethyldithiocarbamate, which is said to be sensitive to 1 part of copper in 50,000,000 parts of water. Interference due to small amounts of iron can be prevented by carrying out the test in ammoniacal solution (pH greater than 9) in the presence of such complexing agents as citrate, tartrate, or better, pyrophosphate. Large quantities of iron are best removed by precipitation in hot solution with ammonia; in the presence of sufficient ammonia and ammonium salts there is no adsorption of copper on the precipitated ferric hydroxide. The yellow colour given by copper can be extracted with certain organic solvents (amy1 or isooamyl alcohol, carbon tetrachloride). Cyanide inhibits the formation of the colour.

These two qualitative tests can be adapted to the quantitative determination of traces of copper. SWOP and her co-workers give a procedure for determining copper in sewage and industrial wastes which involves a preliminary digestion of the sample with concentrated nitric and sulphuric acids, adjustment of a suitable aliquot (containing less than 7 μg of copper) to pH about 2.3 with ammonia, buffering with a malonic acid-sodium hydroxide buffer at pH 2.3 and final extraction with a very dilute solution of dithizone in carbon tetrachloride. Interference due to mercury, bismuth or silver is prevented by shaking the carbon tetrachloride layer with an acid solution of potassium iodide which converts these metals to non-interfering complexes. In this way, concentrations of copper from 0.04-14 p.p.m. can be determined using 25-250 ml. of sample. These authors also used the sodium diethyldithiocarbamate method, the yellow colour being extracted with carbon tetrachloride and determined photometrically. The carbamate method can also be used visually without extracting with carbon tetrachloride, but
although this is simpler in practice, the range is much less, being restricted to amounts of copper between 0·005 mg and 0·05 mg (in 50 ml. Nessler tubes), for, with larger amounts of copper, cloudy solutions tend to be obtained. Jekabury 234, who prefers this method to the extraction procedure, eliminates interference of nickel, cobalt, manganese, iron, lead and cadmium by adding ethylene diamine tetra-acetic acid, which forms complexes with these interfering metals, excess of EDTA being removed with magnesium sulphate.

A new reagent almost specific for copper, namely 2:2'-diquinolyl (2:2'-biquinoline, or 'cuproine') 235, 236, gives promise of being more widely used when it becomes less expensive.

2:2'-diquinolyl

This reagent, which is several times as sensitive as sodium diethyl-dithiocarbamate, gives a purple coloration with traces of cuprous copper (obtained by reduction of cupric copper with hydroxylamine hydrochloride) in neutral or slightly acid solution. Moderate quantities of iron and nickel do not interfere. The determination can be carried out in aqueous solution or the copper complex can be extracted with amyl alcohol. The application of this method to the determination of copper in sewage and trade wastes is described by Butts and his associates 220. A recent paper by Elwell 236A suggests that sulphurous acid is a better reducing agent than hydroxylamine hydrochloride when certain interfering elements (e.g. chromium) are present.

Another almost specific reagent for copper, namely bis-cyclohexanone oxalylidihydrazone, has been proposed by Nilsson 237 and details of its use are given in a publication of Hopkin and Williams 222.

bis-cyclohexanone oxalylidihydrazone

This reagent, which can detect 1 part of copper in 25,000,000 parts of water, gives a blue complex with copper over the range pH
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The reaction is carried out in ammoniacal solution in the presence of ammonium citrate to prevent precipitation of other metal hydroxides. The application of this reagent to the determination of small amounts of copper in pulp and paper has been described by Wetlesen and Gran.

Other reagents have been proposed for the determination of copper, for example dithio-oxamide, and bis-(2-hydroxyethyl) dithiocarbamate, but these do not offer many advantages over the reagents already described.

Iron is found in the ferrous (divalent) and ferric (trivalent) states in iron pickling liquors, ochre waters from coal mines, drainage from coal tips, and galvanizing and wire-drawing wastes. If qualitative tests show that ferrous iron is present, it should be determined quantitatively in such a way as to avoid its oxidation to the ferric state (e.g., direct titration in acid solution with standard dichromate).

A method for estimating ferrous iron in river muds and pollutional sediments is given by Fair, Moore and Thomas.

Numerous reagents are available for the detection and colorimetric estimation of ferrous iron and ferric iron. Potassium ferrocyanide (deep blue colour or precipitate with ferric salts), potassium ferricyanide (deep blue colour or precipitate with ferrous salts), and potassium or ammonium thiocyanate (deep wine-red coloration with ferric salts) have long been used for these purposes but have many disadvantages which have to a considerable extent led to their replacement by some of the newer organic reagents, such as 2:2'-dipyridyl, 1:10-phenanthroline, 2:2':2''-tripyridyl, sulphosalicylic acid, and thioglycollic acid:

2:2'-dipyridyl
1:10-phenanthroline
2:2':2''-tripyridyl

2:2'-dipyridyl gives a red soluble complex with ferrous iron in slightly acid solution but not with ferric iron. The reaction is sensitive and virtually specific. Fluorides, phosphates, and aliphatic
hydroxy-acids, which so markedly affect the detection and determination of ferric iron with thiocyanate, have no effect on the dipyrild reaction. In order to detect or determine ferric iron with dipyrild, a preliminary reduction with hydroxylamine hydrochloride to the ferrous state is necessary.

**1:10-phenanthroline** is very similar to dipyrild and gives a red soluble complex with ferrous iron in slightly acid solution but not with ferric iron.

Sulphosalicylic acid gives a purple coloration with slightly acid solutions of ferric salts. Several anions (fluorides, phosphates, aliphatic hydroxy-acids) interfere by masking the coloration but the only interfering cation is titanium.

The most popular reagents for the colorimetric determination of traces of iron are thiocyanate, thioglycollic acid, 2,2'-dipyrild, and o-phenanthroline. Many waters can be directly examined for iron without any preliminary treatment other than acidification. If much organic matter is present, the sample should be evaporated to dryness, ignited gently, and extracted with concentrated hydrochloric acid to dissolve the iron. Alternatively, a wet oxidation procedure with concentrated nitric and sulphuric acids can be used to destroy organic matter.

Potassium (or ammonium) thiocyanate is still much used for the colorimetric determination of ferric iron and it has the advantages over other reagents of cheapness and of yielding the characteristic wine-red coloration even in quite strongly acid solutions (pH 0.1–2.0). It is necessary to use a large excess of thiocyanate and the colour is not very stable and fades rather easily especially in strong sunlight. Metals which form insoluble thiocyanates interfere with the test and mercuric salts, fluorides, phosphates and organic hydroxy-acids tend to bleach the coloration. Organic solvents stabilize and intensify the colour of the ferric thiocyanate and the determination has been carried out with success in solutions containing 60 per cent of acetone and in methyl cellosolve (2-methoxyethanol) solution. The red ferric thiocyanate can also be concentrated and extracted from aqueous solutions, using such immiscible solvents as diethyl ether, ethyl acetate, amyl acetate, etc. A Lovibond comparator disc for use with the Lovibond comparator is available for this extraction procedure over the range 0.4–5.0 p.p.m. of iron, the ferric thiocyanate being extracted from a 5 ml sample with a mixture of equal volumes of amyl acetate and amyl alcohol.

Thioglycollic acid reacts with both ferrous and ferric iron in ammoniacal solution (pH greater than 8.0) to give a purple coloration, citrate being added to prevent precipitation of metallic hydroxides. The reagent is thus useful for the determination of total iron.
DETECTION AND MEASUREMENT

(i.e. ferrous + ferric). Most anions do not appreciably affect the determination but nickel, cobalt and uranyl salts cause interference and should be removed. Permanent glass colour standards for this method are available for use with (a) the B.D.H. Lovibond nessler-izer, thus permitting the determination of iron over the range 0.04–1.2 p.p.m. of iron (50 ml samples), and (b) the Lovibond comparator, covering the range 2–20 p.p.m. of iron (5 ml samples).

Dipyridyl and phenanthroline determine ferrous iron only and ferric salts must first be reduced to the ferrous state. The red colour is stable over the pH range 3–9 and is not subject to so many interferences as the thiocyanate colour. Amounts of iron as low as 0.05 p.p.m. can easily be determined visually. Butts and his co-workers separate iron from interfering substances, prior to a determination with o-phenanthroline, by a preliminary extraction of ferric chloride from hydrochloric acid solution with di-isopropyl ether.

Several derivatives of o-phenanthroline have been prepared, the most sensitive being bathophenanthroline or 4:7-diphenyl-1:10-phenanthroline, which is specific for iron. This reagent forms a stable red complex with ferrous iron at pH about 4.0. The colour can be extracted with isoamyl alcohol or n-hexyl alcohol and the colour intensity measured spectrophotometrically or visually. As little as 0.001–0.01 p.p.m. of iron can be accurately determined in this way.

Another very sensitive reagent for iron is 2:2':2":3"-tripyridyl. This compound gives a reddish-purple stable complex with ferrous iron over the pH range 1.5–12.0. Interfering heavy metals are sequestered by buffering with ethylene diamine at pH about 9.6. The determination can be carried out photometrically or visually; in the latter case, using 100 ml samples in Nessler tubes, iron can be estimated over the range 0.005–2.0 p.p.m. The reagent is unfortunately extremely expensive in this country. The method has been tentatively recommended for iron in the latest revision of the A.P.H.A. Standard methods for the examination of water, sewage and industrial wastes.

When the quantities of iron present are too large for colorimetric determinations, volumetric methods are satisfactory. Thus, ferrous iron can be accurately determined by titration with standard potassium dichromate (0.1, 0.01 or even 0.001 N) in hydrochloric acid or sulphuric acid solutions, using diphenylamine, diphenylamine sulphonic acid, N-phenylanthranilic acid, or 1:10-phenanthroline as internal indicators. If ferric iron is to be determined in this way, it must first be reduced to the ferrous condition with stannous chloride.

* Phosphoric acid must also be present if these indicators are used.
The dichromate titration of ferrous iron may give inaccurate results in the presence of easily oxidizable organic matter. In such cases, to avoid interference by organic matter, use can be made of a modification due to Heisig\textsuperscript{245} of the Andrews-Jamieson method in which standard potassium iodate is used as titrant in the presence of high concentrations of hydrochloric acid and an organic solvent (chloroform or carbon tetrachloride)\textsuperscript{246-248}. The acidity at the end of the titration must be about 3-4 s, otherwise the iodine monochloride formed is partially hydrolysed. Owing to the easy oxidation of ferrous salts by air in strong hydrochloric acid solutions, excess of iodine monochloride is added to oxidize the ferrous iron before addition of acid, then strong hydrochloric acid is added and the iodine formed is titrated with standard potassium iodate in a stoppered bottle with vigorous shaking in the presence of a layer of carbon tetrachloride. At the end-point, the organic solvent layer loses its purple colour:

\[
\begin{align*}
2\text{FeSO}_4 + 2\text{ICl} + 4\text{HCl} & = 2\text{FeCl}_3 + \text{I}_2 + 2\text{H}_2\text{SO}_4 \\
2\text{I}_2 + \text{KIO}_3 + 6\text{HCl} & = \text{KCl} + 3\text{ICl} + 3\text{H}_2\text{O}
\end{align*}
\]

Smith and Wilcox\textsuperscript{249} have shown that amaranth can with advantage be used as internal indicator (best added towards the end of the titration) in place of the organic solvent, the colour change being from red to colourless.

**Lead**\textsuperscript{1-4}

Lead is present in rivers whose watersheds contain lead mines, in effluents from the manufacture of accumulators, in lead paint wastes, and wastes from the manufacture of pewter ware. Lead compounds are toxic to all forms of life.

If present in not too small amounts (greater than 2 p.p.m.) lead can be detected by Feigl’s test with sodium rhodizonate which forms a coloured inner complex salt with lead\textsuperscript{94}:

\[
\begin{align*}
\text{O} & \quad \text{ONa} \\
\text{O} & \quad \text{ONa}
\end{align*}
\]

To carry out the test, a drop of the sample is placed on filter paper and the spot touched with a drop of freshly prepared aqueous sodium rhodizonate. In the presence of lead a blue colour is formed which changes to scarlet on adding a drop of buffer solution, pH 2-8. Even very sparingly soluble compounds of lead (e.g. lead
sulphate) respond to this test. If the lead is first separated by precipitation as lead sulphate, the test becomes quite specific for lead since any co-precipitated barium sulphate does not react. The detection of traces of lead (down to about 0-01 p.p.m.) is best done with dithizone. The sample containing Rochelle salt and potassium cyanide is shaken with a 0.002 per cent solution of dithizone in carbon tetrachloride when the green colour of the reagent changes to red in the presence of lead. Only bismuth and the rare element thallium interfere with this test.

Prior to the more widespread use of the dithizone procedure, a popular method used in this country for the determination of small amounts of lead was the sulphide method. This method depends upon the formation of brownish colloidal lead sulphide when sodium sulphide is added to an ammoniacal lead solution in the presence of ammonium citrate (which prevents the disturbing effect of aluminium, calcium and magnesium salts on the coloration) and potassium cyanide (which prevents interference by copper and by small amounts of iron by converting these metals to complex cyanides). For accurate work, and when organic matter is present, the lead is isolated, after a wet digestion with nitric and sulphuric acids, by precipitation with hydrogen sulphide as lead sulphide. This precipitate, which may also contain copper and traces of iron, is dissolved in nitric acid, converted to insoluble lead sulphate by precipitation with sulphuric acid in an alcohol-water medium, the lead sulphate is then dissolved in ammonium acetate and the lead estimated colorimetrically as sulphide. The colour comparison is simplified by using the appropriate disc supplied for use with the B.D.H. Lovibond nesslerizer, which covers the range 0-4-4 p.p.m. of lead (if a 25 ml. aliquot is taken). GAD has applied the sulphide method directly as a field test to potable waters without any preliminary treatment, and states that using 100 ml. samples in Gehner cylinders, as little as 0·02 p.p.m. of lead can be estimated.

The determination of traces of lead (down to about 0·01 p.p.m.) is best carried out by extracting the slightly ammoniacal sample (pH about 8·5-10) with a carbon tetrachloride solution of dithizone in the presence of sodium citrate and potassium cyanide, only bismuth and thallium, which are unlikely to be present, interfere. Any interference by ferric iron, which oxidizes dithizone, is prevented by addition of hydroxylamine hydrochloride.

Manganese

Manganese compounds are not normally toxic to plants and animals, with the exception of the purple-coloured permanganates which have bactericidal properties.
drenage can be objectionable on account of the brown precipita-

tion of manganic hydroxide which is produced when the drainage reacts with the natural alkalinity of the stream. Manganese compounds can also occur in chemical waste waters where they are often associated with lime sludges.

The following tests can be used for the detection of manganese:

(a) A drop of the sample containing Mn$^{II}$ is placed on filter paper, made alkaline with dilute caustic soda, and then after waiting a few seconds to permit oxidation of the manganous hydroxide to manganic hydroxide by air, a drop of a solution of benzidine in dilute acetic acid is added. In the presence of manganese, a blue or blue-green coloration is obtained. Interference due to iron is prevented by adding Rochelle salt$^{44}$. Other oxidizing agents (e.g. chromates and permanganates) react similarly. Lime sludges containing manganese in the oxidized form respond to the test without adding any alkali.

(b) When samples containing manganese in any state of valency are evaporated to dryness and fused with sodium carbonate and a little potassium nitrate, a green mass is obtained due to the formation of sodium manganate:

$$
\text{MnO} + \text{O}_2 + \text{Na}_2\text{CO}_3 = \text{Na}_2\text{MnO}_4 + \text{CO}_2
$$

This is a very sensitive and specific test for any manganese compound$^{49}$.

(c) A drop of the neutral sample is treated with a drop of saturated potassium periodate, a drop of dilute acetic acid, and then 2 drops of a solution of tetramethyl-$p$-diaminodiphenylmethane in chloroform. Permanganate is formed by oxidation and reacts with the amine giving a blue colour$^{44}$. This test will detect 0.001 μg of manganese, or 1 part of manganese in 50,000,000 parts of water.

The determination of manganese is generally carried out by boiling the sample with excess of potassium periodate in the presence of sulphuric acid, or if iron is present, a mixture of sulphuric and phosphoric acids$^{2,7,220}$. Unless the sample is low in chlorides and organic matter, a preliminary digestion with nitric and sulphuric acids is necessary to destroy organic matter and remove chlorides. Small amounts of silver nitrate catalyse the oxidation of manganese with periodate and are specially desirable if only traces of manganese are present. The intensity of the colour of the permanganate produced is measured photometrically or by comparison with standards. As little as 0.01 p.p.m. of manganese can be estimated in this way.

An alternative method of oxidizing manganese to permanganate
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is by means of ammonium persulphate in acid solution using silver nitrate as a catalyst. According to Sandell\(^9\), the reaction should be carried out in the presence of nitric and phosphoric acids and reasonable amounts of organic matter do not interfere if extra persulphate is used and the period of heating is longer. Mercuric sulphate can be added to prevent interference of chlorides. According to Nydalh\(^2\), persulphate is superior to periodate as an oxidizing agent for traces of manganese.

Mercury

Mercury compounds, which are extremely toxic to all forms of life, including bacteria, may be present in waste waters from the manufacture of insecticides and fungicides, and in 'white water' from paper mills using mercury compounds (such as phenyl mercuric acetate) to prevent slime formation.

In dilute nitric acid solution, monovalent and divalent mercury salts give a purple-blue coloration with diphenylcarbazide\(^8\). Interference due to molybdates is avoided by complexing with oxalic acid, while if chromates are present they can be reduced to the un-reactive trivalent state by sulphur dioxide. Dithizone affords a much more sensitive test for mercury. When mercurous or mercuric salts in dilute mineral acid solution (preferably sulphuric acid about normal in strength) are shaken with a chloroform or carbon tetrachloride solution of dithizone, the green colour of the reagent changes to yellow or orange. Among the commoner metals, only silver and copper interfere, while among the anions chlorides should not be present in appreciable amounts since they form complexes with mercury.

Dithizone was used by Johansson\(^2\) for the colorimetric determination of mercury in 'white water' from paper mills. The water was treated with hydrogen sulphide and the precipitated mercury sulphide was digested with a mixture of nitric and sulphuric acids and the solution, after adjustment to pH 1-6, was extracted with a solution of dithizone in chloroform.

Nickel

Nickel occurs in many electroplating wastes. It is toxic to fish and other river life, and has an adverse effect on biological sewage treatment processes (page 493) and on sludge digestion (page 466)

The classical test for nickel, namely the red precipitate or colour formed with an alcoholic solution of dimethylglyoxime\(^2\).
in ammoniacal solutions (or with the water soluble sodium salt of dimethylglyoxime), is one of the oldest examples of the use of an organic reagent for the detection of a metal, and will detect 1 part of nickel in 2,000,000 parts of water. A more sensitive test, detecting 1 part of nickel in 5,000,000 parts of water, is provided by ‘nioxime’ or 1:2-cyclohexanedione dioxime.

\[
\begin{align*}
\text{CH}_2 & \\
\text{CH}_2 & =\text{NOH} \\
\text{CH}_2 & =\text{NOH} \\
\text{CH}_2 &
\end{align*}
\]

This is used as a 0.8 per cent aqueous solution and reacts with nickel in slightly acid (pH 3.0), neutral or ammoniacal solutions to give a purple-red colour or precipitate. If iron is present, the reaction with either dimethylglyoxime or with nioxime should be carried out in ammoniacal tartrate solution.

These tests for nickel fail in the presence of cyanide. A sensitive test for nickel in the presence of cyanide has been described by Feigl. The sample is mixed with bromine water, rendered alkaline with ammonia, and then treated with an alcoholic solution of dimethylglyoxime when a reddish-brown coloration appears due to the formation of a complex compound of tetravalent nickel. This test can be made the basis of a quantitative method for the determination of nickel in amounts covering the range 0.1-1.0 p.p.m.

The presence of ammonium tartrate prevents interference of iron. The separation of nickel from many elements interfering with this method can be achieved by making use of the solubility of the nickelous compound of dimethylglyoxime in chloroform. By extracting a faintly ammoniacal solution containing citrate or tartrate in this way, nickel can be separated from ferric iron, aluminum, cobalt and a number of other elements. Although some copper is also removed by the chloroform extraction, washing the extract with dilute ammonia dissolves the copper leaving the nickel in the chloroform layer. The chloroform extract containing the nickel dimethylglyoxime is then shaken with dilute hydrochloric acid whereby the nickel passes to the aqueous phase and can then be determined colorimetrically by the bromine-dimethylglyoxime procedure; this method has been used (after destruction of organic matter) by Riehl for the determination of nickel in sewage and sewage sludges, and by Gardner, Serfas and Muraca for the determination of nickel in plating waste waters.

Selenium may occur in waters draining selenium-containing soils
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or rocks (e.g. in parts of the U.S.A.). It is used commercially in
the manufacture of some photo-electric cells. Selenium and sele­
nites are toxic to living organisms. Selenium compounds emit a
peculiar odour reminiscent of decaying radishes when heated with
sodium carbonate upon charcoal.

A sensitive test for selenites, detecting 1 p.p.m. of selenium or
even less, is described by Feigl. The sample acidified with hydro­
chloric acid is treated with excess of a freshly prepared 1 per cent
solution of α-diphenylhydrazine in glacial acetic acid when a red­
violet coloration soon appears. Selenium should first be reduced
to selenites by boiling with concentrated hydrochloric acid. Any
interference by ferric iron and cupric copper is prevented by adding
oxalic acid.

The A.P.H.A. give a tentative method for the estimation of
selenium in the range 0.01–0.5 p.p.m. using 1 l. of sample. The
sample (after treatment with sodium peroxide and evaporation) is
distilled with hydrobromic acid, bromine, and sulphuric acid, when
volatile selenium tetrabromide passes over and is hydrolysed in
aqueous solution to selenious acid. After removing excess of
bromine with sulphur dioxide, the selenious acid is reduced by
means of hydroxylamine hydrochloride to red colloidal selenium
which is matched visually against standards:

\[ \text{H}_2\text{SeO}_3 + 2\text{NH}_2\text{OH} \cdot \text{HCl} = \text{Se} + \text{N}_2\text{O} + 4\text{H}_2\text{O} + 2\text{HCl} \]

Another method suitable for traces of selenium (0.1–5.0 p.p.m.) in
water has been described by Lambert and his associates. The
selenium is converted to selenious acid by means of sulphuric acid,
potassium bromide and sodium hypochlorite, and, after removal of
the excess of bromine, the selenious acid is allowed to react with
cadmium iodide and the liberated iodine determined colori­
metrically.

Silver occurs in waste waters from the manufacture of photographic
chemicals, often as insoluble silver chloride or bromide. It is very
toxic to fish and other river life, including bacteria.

A sensitive qualitative test for traces of silver utilizes the purple­
red colour given by silver ions in approximately n/10 nitric acid
solution with a dilute acetone solution of p-dimethylamino–benzal­
rhodanine.

Reliable methods for the determination of traces of silver are few.
If present in solution, probably the best method is based upon the
yellow keto dithizonate formed when the silver solution is shaken
with a chloroform or carbon tetrachloride solution of dithizon in
the presence of 0.5–1 N sulphuric acid, but mercury interferes.
Interference due to copper is avoided, according to Sandell, by employing cupric dithizonate as reagent instead of dithizone and a 'mixed colour' method of colour comparison is then used, the colours ranging from violet to yellow.

If silver is present as insoluble bromide or chloride, the precipitate is dissolved in ammonia, and the dilute ammoniacal solution is reduced with sodium hydrosulphite (sodium dithionite, Na₂S₂O₄), when yellow colloidal silver is formed which can be estimated colorimetrically. According to Gad and Naumann, the method is suitable for concentrations of silver ranging from 0.1-0.5 p.p.m.; with higher silver concentrations the colloidal silver tends to precipitate but addition of gum arabic as protective colloid enables the method to be used up to concentrations of silver of 2 p.p.m.

Titanium occurs in waste waters from the manufacture of titanium dioxide and titanium pigments and also as white insoluble titanium dioxide in paper mill effluents using titanium dioxide as a 'filler'. Titanium compounds are not, so far as is known, toxic to fish and other river life and are objectionable chiefly when present as suspended matter.

The detection of titanium is generally carried out by evaporating the sample to dryness, igniting to destroy organic matter, fusing the ash with potassium bisulphate to convert titanium dioxide to titanic sulphate, dissolving the product in dilute sulphuric acid and adding hydrogen peroxide when a stable yellow or orange coloration is obtained. Addition of phosphoric acid in this test prevents interference by iron. By adding fluoride the colour is bleached, owing to the formation of stable [TiF₆]₃⁻ ions.

Another sensitive qualitative test for titanium, described by Feigl, involves treatment of the sample, or residue obtained on evaporation, with excess of a 0.1 per cent solution of chromotropic acid in concentrated sulphuric acid when a violet coloration is obtained.

The determination of titanium is usually carried out by the hydrogen peroxide method on the solution obtained by leaching the potassium bisulphate melt with dilute sulphuric acid. As little as 1 p.p.m. of titanium can be determined visually by this colorimetric method in 50 ml. Nessler tubes. Vanadium, chromium and molybdenum interfere. If these elements are present, the sample is evaporated to dryness, fused with sodium carbonate and a little sodium nitrate, and the melt on cooling is leached with hydrogen peroxide to remove vanadate, chromate and molybdate. The titanium remains as insoluble titanium dioxide, which can be fused with potassium bisulphate and estimated by the hydrogen peroxide method.
For the determination of still smaller quantities of titanium (in the range 0.01 - 0.8 p.p.m.) use can be made of disodium 1,2-dihydroxy-3,5-disulphonate which gives an intense yellow colour with tetravalent titanium over the pH range 4.3 - 9.6. Interference due to iron is prevented by carrying out the reaction in an acetic acid–sodium acetate buffer at pH 4.7 and reducing the iron to the unreactive ferrous condition with sodium hydrosulphite (sodium dithionite, Na₂S₂O₄). Fluorides interfere, and molybdates and uranyl salts must be absent since they give yellow colours with the reagent.

**Uranium**

Uranium compounds are highly toxic and may be present in waste waters from the processing of uranium minerals and ores and in discharges from atomic energy plants. A publication of the Department of Scientific and Industrial Research gives an account of chemical methods available for the determination of macro and micro quantities of uranium, and Sandell describes colorimetric methods suitable for trace amounts of uranium such as are likely to occur in waste waters. When using colorimetric methods it is usually advisable to separate uranium from interfering elements by making use of the fact that uranyl nitrate [UO₂(NO₃)₄] can be extracted quantitatively by ether from an aqueous solution containing nitric acid and ammonium nitrate.

The thiocyanate method of Currah and Beamish depends upon the yellow coloration produced when ammonium thiocyanate is added to an acid solution of a uranyl salt; interference due to iron is obviated by adding stannous chloride which reduces ferric iron to ferrous iron. Molybdenum must be absent as even traces interfere by giving a yellow-orange colour.

A reagent about five to six times as sensitive as thiocyanate for the determination of uranium is dibenzoylmethane (C₆H₅CO·CH₂·CO·C₆H₅) which according to Yox and his co-workers gives a bright yellow stable coloration with uranyl salts over the pH range 6.5 - 8.5. By using 50 ml. Nessler tubes (tall form) as little as 0.05 p.p.m. of uranium can be estimated. If interfering ions (e.g. iron, molybdenum and vanadium) are present, the ether extraction procedure should be used for the separation of the uranium.

Very small amounts of uranium (down to about 3 µg) can be determined polarographically. The most sensitive method for traces of uranium is based upon the intense yellow-green fluorescence given by uranium compounds when fused with sodium fluoride. This fluorophotometric method will determine as little as 0.001 - 10 µg of uranium, but many elements interfere and must be removed.
The fluorescence test is also the most sensitive qualitative test for traces of uranium and is best carried out by examination in ultraviolet light.

**Vanadium**

Vanadium occurs frequently in certain Argentine waters. Its compounds are toxic and find some uses in industry but are not commonly present in trade wastes.

The common vanadium compounds are the blue vanadyl salts in which vanadium is tetravalent (e.g. vanadyl sulphate, $\text{VOSO}_4$, containing the divalent $\text{VO}^{2+}$ ion) and the vanadates (e.g. sodium vanadate, $\text{NaVO}_3$) in which the element is pentavalent. Vanadyl salts are converted by oxidizing agents (such as bromine water, acid permanganate) to vanadates, and the latter can be reduced back again to vanadyl compounds by reducing agents (e.g. passage of sulphur dioxide through hot dilute sulphuric acid solutions, or evaporation with concentrated hydrochloric acid).

Belcher and his co-workers have described a test for vanadates based upon the red-violet colour given by vanadates in sulphuric acid solution with a 1 per cent solution of 3:3'-dimethyl-naphthidine in glacial acetic acid. When carried out as a spot test, as little as 2 p.p.m. of vanadium can be detected. Other oxidizing agents (e.g. chromates, permanganates) must be absent since they react in a similar way. The most sensitive qualitative test for vanadium (detecting 0-1 p.p.m. or even less) is that described by Bach and depends upon the reaction between vanadates and 8-hydroxy-quinoline in dilute acetic acid solution to give a violet-black complex $(\text{C}_9\text{H}_6\text{O}_7\text{N})_4\text{V}_2\text{O}_7$, which can be extracted by isoamyl alcohol giving a red solution. This test can be adapted to the quantitative determination of vanadium. A Lovibond comparator disc is available for the visual determination by this method, enabling as little as 0-2 p.p.m. of vanadium to be determined in a 50 ml sample. Interference due to limited amounts of iron (up to 100 $\mu$g) can be prevented by adding sodium pyrophosphate and interference from titanium by adding sodium fluoride. Copper interferes and must be removed.

A volumetric method for determining vanadium in quantities ranging from 10-1000 p.p.m. has been described by Swope, Hattman and Pellkofer; it involves oxidation of the vanadium to vanadate by means of permanganate, addition of a known excess of ferrous sulphate, and back-titration with 0-006N ceric sulphate.

**Zinc**

Zinc is found in zinc-mine wastes and in rivers in the vicinity of such mines, in wastes from factories making zinc compounds, in
zinc plating wastes, galvanizing wastes, viscose rayon wastes, and wastes from the manufacture of rubber. Zinc compounds are very toxic to fish.

Although numerous satisfactory reagents, which are almost specific or at any rate highly selective, are available for most of the common metals found in trade wastes and river water, there is a scarcity of good tests for small amounts of zinc.

One of the oldest tests for zinc depends on the white turbidity obtained when the acidified sample is treated with a solution of potassium ferrocyanide. The turbidity is caused by the formation of insoluble potassium zinc ferrocyanide and as little as 0.4 p.p.m. of zinc can be detected in a colourless water. More than traces of iron and copper as well as metals forming sparingly soluble ferrocyanides cause interference.

The most satisfactory test for traces of zinc is based upon the use of dithizone. On shaking a sample with a 0.001 per cent solution of dithizone in carbon tetrachloride for about 2 minutes, the green colour of the reagent changes to violet or red if zinc is present. According to Fischer and Leopold interference by other heavy metals (e.g., copper, cadmium, lead, silver and mercury) is prevented by carrying out the test at pH 4.5-5.0 in the presence of sodium thiosulphate. This procedure is now generally used for the estimation of zinc in amounts down to about 0.01 p.p.m. Modifications of the method have been applied by Butts and his associates to the colorimetric determination of zinc in sewage and trade wastes and by Muraca and his co-workers to the colorimetric determination of zinc in plating waste waters.

The ferrocyanide method has been much employed in the past for the turbidimetric estimation of zinc in potable waters; the procedure is only satisfactory in the case of clear colourless waters of low organic content and containing less than 1 p.p.m. of iron and less than 0.5 p.p.m. of copper. Rush and Yoe have recently discovered a sensitive new reagent for zinc with the rather formidable names L-2-(a-(2-hydroxy-3-sulphophenylazo)-benzylidene) hydrazino] benzoic acid, or, 2-carboxy-2'-hydroxy-3-sulphoformazylbenzene. It has the following structure,
and the authors wisely propose to call it ‘zincon’ for short. Zinc in alkaline solution (pH 8.5-9.5) and copper at pH 5.0-9.5 both give a blue colour with the reagent but owing to the difference in the effect of pH on the colour formation it is possible to estimate zinc and copper in the presence of each other since only copper reacts in slightly acid solution. In the determination of zinc in a solution buffered at pH 9.0, Beer’s law is followed over the range 0.1-2.4 p.p.m. of zinc. Although the reagent is not quite so sensitive as dithizone, it has the advantage of avoiding tedious extraction. If appreciable amounts of interfering metals are present (e.g. iron, chromium, manganese and nickel), it is advisable to separate the zinc with an ion-exchange resin.

**Cyanide**

Cyanides are likely to occur in dangerous concentrations in waste waters from electroplating, gold-mining and gilding, in waste waters from the case-hardening of steel, in effluents from gas works and coke ovens, in wastes from the surface cleaning of various metals with cyanides, and in effluents from the scrubbing of gases produced from blast furnaces.

In view of the extremely toxic effects of cyanides on fish (as little as 0.03 p.p.m., expressed as HCN, can be fatal) the importance of using very sensitive as well as specific methods for the detection and estimation of cyanides needs little emphasis.

Cyanide can be present as ‘free cyanide’, for instance as HCN and the simple metallic cyanides like KCN or NaCN. Less frequently, it is present in the form of stable complex cyanides, such as K₄Fe(CN)₆ and K₃Co(CN)₆, which do not exhibit the reactions of the simple cyanides, but some complex cyanides (e.g. potassium zinc cyanide) are relatively unstable and do show the reactions of the simple cyanides. If so-called ‘total cyanide’ (i.e. ‘free cyanide’ plus cyanide present as complex salts) is required, the complex cyanide must first be broken down to a simple cyanide by a distillation procedure, for instance distillation with a hydrochloric acid solution of cuprous chloride¹, or distillation with phosphoric acid in the presence of citric acid and ethylene diamine tetra-acetic acid². The presence of free cyanide generally betrays itself by a characteristic bitter almond odour but unfortunately many persons are relatively insensitive to this smell (see page 54). A modification of the Prussian blue test suggested by Rathneshwara²⁷⁷ will detect as little as 0.1 p.p.m. of HCN; a strip of filter paper is treated with a drop of 10 per cent ferrous sulphate and a drop of 10 per cent caustic soda, and is suspended for about 10 minutes over the acidified sample in a glass-stoppered flask when the liberated HCN diffuses
DETECTION AND MEASUREMENT

and reacts to form ferrocyanide on the paper so that when the paper
is immersed in hot dilute hydrochloric acid a blue or blue-green
stain of Prussian blue appears.

Smaller quantities of cyanide can be detected by the benzidine-
pyridine method of Aldridge,278 which, according to Krawczyk,279, gives a perceptible orange coloration with as little as 0.1
p.p.m. of HCN using a 100 ml. sample.

The Aldridge method278 is one of the best methods for the estima-
tion of traces of cyanide; it is an example of the König synthesis280
in which cyanogen bromide (or chloride) gives a dye by reaction
with pyridine and an aromatic amine (cf. under Tar Bases, page 327).
The cyanide is first converted to cyanogen bromide by means of
bromine water in dilute acetic acid solution:

\[
\text{HCN} + \text{Br}_2 = \text{CNBr} + \text{HBr}
\]

After removing the excess of bromine with sodium arsenite, the
cyanogen bromide is allowed to react with pyridine and benzidine
in dilute hydrochloric acid solution; a quaternary compound of
cyanogen bromide and pyridine is formed which condenses with
benzidine to give a di-anil derivative having an intense orange to
red colour which can be determined photometrically or by com-
parison with standards.1,16. Discs designed for use with both the
Lovibond comparator and the B.D.H. Lovibond nesslerizer can be
applied to the visual determination within the range 0.01–1.0
p.p.m. of HCN. The method can usually be applied without any
preliminary distillation procedure since the complex cyanides of
zinc, cadmium and copper react easily. Thiocyanate reacts in
the same way as cyanide (since it is also converted to CNBr by
bromine). Hence if both cyanide and thiocyanate are present,
the determination should be repeated after the sample has been
aerated to remove cyanide as volatile HCN. Cyanide can also be
separated from thiocyanate (as well as from complex cyanides) by
extraction from acid solution as HCN with isopropyl ether and can
then be recovered from the ether extract by shaking with aqueous
sodium hydroxide.278

If the sample is coloured and turbid, or contains interfering sub-
stances, or has a very low content of cyanide, the modification of
Aldridge’s method suggested by Nussbaum and Skuper281 can be
used with advantage; this involves the extraction of the orange
colour with n-butyl alcohol and permits the determination of
cyanide in polluted waters containing only 0.02–0.5 p.p.m. of
HCN.

Another very sensitive method for cyanide based upon the König
synthesis is due to Epstein282, 283, 215. The cyanide is converted
by chloramine-T to cyanogen chloride which is allowed to react
with pyridine containing 1-phenyl-3-methyl-5-pyrazolone and a small proportion of bis(1-phenyl-3-methyl-5-pyrazolone) to give a blue colour which is said to be more stable than the colour produced in the Aldridge method. The procedure is recommended in the latest revision of the A.P.H.A. *Standard Methods* but the reagents are not easily obtainable in this country.

Other colorimetric methods for determining cyanide are based on the formation of red ferric thiocyanate and on the production of Prussian blue but these procedures are rather time-consuming and not very sensitive. Methods involving the oxidation in alkaline solution (pH 10–11) of phenolphthalein or cresolphthalein to the corresponding red phthalein by cupric ions in the presence of cyanide were popular at one time but unfortunately are not specific for cyanide. The method was, however, applied by the Water Pollution Research Laboratory in a special investigation involving the determination of concentrations of cyanide as low as 0.05 p.p.m., the pink colour being measured in 20 cm cells in a Spekker absorptiometer.

One of the oldest volumetric methods for determining cyanides is that of Liebig in which the cyanide solution is titrated with silver nitrate to form a soluble complex alkali argentocyanide:

\[ 2 \text{KCN} + \text{AgNO}_3 = \text{KAg(CN)}_2 + \text{KNO}_3 \]
or,

\[ 2\text{CN}^- + \text{Ag}^+ = (\text{Ag(CN)}_2)^- \]

When all the cyanide has reacted, the slightest excess of silver nitrate produces a turbidity due to precipitation of silver cyanide:

\[ \text{KAg(CN)}_2 + \text{AgNO}_3 = 2\text{AgCN} + \text{KNO}_3 \]

The completion of the first stage (i.e. the formation of the alkali argentocyanide) is thus indicated by the first appearance of a turbidity. This end-point is not always easy to see especially if the sample is not clear. To overcome this difficulty, a simple modification first proposed by Ryan and Culshaw can be used; the titration of the cyanide, adjusted to pH 10–11 with sodium hydroxide, is carried out in the presence of a few drops of a dilute solution of p-dimethylaminobenzylidene-rhodanine in acetone, when at the end-point the slightest excess of silver nitrate causes a colour change from yellow to salmon-pink. As little as 1 p.p.m. of HCN can be determined by this method (using a micro-burette and a dilute standard silver nitrate), whilst high concentrations are determined by using stronger silver nitrate. Chlorides do not interfere with the method.

**Thiocyanate**

Thiocyanates may be present in gas liquor from a gas works but the amounts are nowadays usually small.
DETECTION AND MEASUREMENT

Thiocyanates can be detected by the wine-red coloration they give with ferric chloride in hydrochloric acid solution (compare test for ferric iron, page 305). This test can be made the basis of an approximate colorimetric determination; cyanides do not interfere but mercury salts, fluorides and organic hydroxy-acids should be absent. As already indicated (page 319), Aldridge’s method can be used for the determination of traces of thiocyanate; if cyanide is present, it can be removed by aerating the sample acidified with acetic acid.

A colorimetric method for thiocyanate sensitive to 0.5 p.p.m. of CNS or even less has been described by Kruse and Mellon and is based upon the formation of a complex copper pyridine thiocyanate, Cu(C₅H₅N)₂(CNS)₂, which can be extracted by chloroform to yield a yellow solution. Cyanide interferes and must be removed.

If thiocyanate is present in fair quantity, it can be estimated by precipitation as cuprous thiocyanate which is titrated with standard potassium iodate in fairly concentrated hydrochloric acid solution in the presence of chloroform (an adaptation of the Andrews–Jamieson method).

FORMALDEHYDE

Formaldehyde occurs in wastes from the manufacture of synthetic resins and plastics, in some tannery wastes and in penicillin wastes. It is a reducing agent and strongly bactericidal, and is, therefore, an undesirable constituent of river waters.

Formaldehyde gives a blue to greenish-blue colour with a 0.5 per cent solution of carbazole in pure concentrated sulphuric acid. This test, which can detect as little as 0.01 mg of formaldehyde, can be carried out either as a spot test, or better, in a test-tube as a ‘ring’ test in such a way that the carbazole-sulphuric acid reagent forms a layer underneath the sample.

A specific test for formaldehyde not given by other aldehydes is described by Feigl. It depends on the violet colour produced when formaldehyde is heated at 60°C for about 10 minutes with a fairly concentrated sulphuric acid solution of chromotropic acid (1:8-dihydroxynaphthalene-3:6-disulphonic acid).

Methods for the colorimetric determination of small amounts of formaldehyde are reviewed by Reynolds and Irwin. The method using chromotropic acid appears to be the most specific and involves heating the sample with chromotropic acid in 72 per cent sulphuric acid at 60°C for 10 minutes, or in a boiling water bath for 30 minutes, and comparing the violet colour with that of a
series of standards, or measuring it absorptiometrically. Most other aldehydes, with the exception of acrolein, do not interfere unless present in large proportion. As little as 1 p.p.m. of formaldehyde can be estimated by this method.

Schryver's method for determining formaldehyde, though not so specific as the chromotropic acid procedure, is easier to carry out and is more sensitive. It is based upon the intensity of the magenta colour obtained when very dilute solutions of formaldehyde are treated with phenylhydrazine hydrochloride and potassium ferricyanide and then acidified with hydrochloric acid. The colour can be compared with that of a series of standards, or measured absorptiometrically. In a recent modification of the method, the colour is extracted with n-butyl alcohol, and determined photometrically at 520 μ, thus enabling formaldehyde to be estimated in the range 0·1-0·7 p.p.m. even in the presence of iron which normally interferes.

PHENOLS ('Tar acids')

Phenols are derivatives of benzene and other aromatic hydrocarbons in which one or more hydroxyl groups replace hydrogen atoms and so are directly attached to the aromatic ring. Phenols thus contain one or more of the > C—OH groups; if one hydroxyl group is present, the phenol is said to be 'monohydric', if more than one hydroxyl group is present, the phenol may be dihydric, trihydric, etc., or more generally 'polyhydric'. A few typical examples of phenols are given in Table 57.

Ordinary phenol, the three cresols, the xylenols, as well as many polyhydric phenols are present in coal-tar and gas liquor. Phenols are also found in synthetic resin and plastics wastes, rubber-proofing wastes, cutting-oil wastes, drainage from tarred roads, commercial disinfectants, many chemical wastes, dye manufacturing wastes, and certain wastes from the dyeing and finishing of rayon (where phenols are used as delustering agents).

The presence of phenols in a stream is objectionable because of their strong bactericidal action, their toxicity to fish and the unpleasant tastes and odours produced when water containing phenols is chlorinated (cf. page 52).

Phenols generally impart to a sample a characteristic 'disinfectant' odour. One of the oldest tests for phenols is the Millon reaction in which the sample is heated with a freshly prepared solution of mercury in nitric acid when, in the presence of phenols, a red colour develops. In place of Millon's reagent, which does not
**DETECTION AND MEASUREMENT**

**Table 57. Typical examples of phenols**

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<th>Monohydric phenols</th>
<th>Dihydric phenols</th>
<th>Trihydric phenols</th>
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<tr>
<td>Phenol, $C_6H_5OH$ or $\text{CH}_3\text{C}_6\text{H}_4\text{OH}$</td>
<td>Catechol</td>
<td>Pyrogallol</td>
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<td>Cresols, $C_7H_8O_3$</td>
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<td>(3 isomers)</td>
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*Note: The images of the molecular structures are not provided in the text.*
not keep well, Nasse\textsuperscript{297} recommends the employment of an aqueous solution of mercuric acetate, to which a few drops of dilute sodium nitrite and of dilute acetic acid are added when the test is to be performed. Another sensitive test for phenols, first applied to proteins containing tyrosine, is due to Folin and Ciocalteu\textsuperscript{298} who use a reagent containing a mixture of phosphotungstic and phosphomolybdic acids which is reduced by phenols in the presence of sodium carbonate to blue products of lower valency. The method can be adapted to quantitative work\textsuperscript{90} but unfortunately is not specific for phenols as many other reducing compounds behave in a similar way.

A useful review of methods for the quantitative determination of phenols is given in the \textit{Chemical Age}\textsuperscript{299}. For many years, the standard method used in this country for the estimation of phenols (monohydric as well as polyhydric)* has been that of Fox and Gauge\textsuperscript{300}. This involves the coupling of the phenol in caustic soda solution with freshly diazotized sulphanilic acid, obtained by the action of sodium nitrite on a cooled solution of sulphanilic acid in dilute sulphuric acid. A yellow or orange azo dyestuff is thus produced; in the case of phenol itself the reactions taking place can be represented by the following equations:

\begin{align*}
\text{Diazoization:} & \quad 2\text{SO}_3\text{H}^+\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2 + 2\text{HNO}_2 + \text{H}_2\text{SO}_4 \\
& = 4\text{H}_2\text{O} + (\text{SO}_3\text{H}^+\cdot\text{C}_6\text{H}_4\text{N}_2)\text{SO}_4
\end{align*}

\begin{align*}
\text{Coupling:} & \quad (\text{SO}_3\text{H}^+\cdot\text{C}_6\text{H}_4\cdot\text{N}_2)\text{SO}_4 + 2\text{C}_6\text{H}_5\text{OH} \\
& = \text{H}_2\text{SO}_4 + 2\text{SO}_2\text{H}^+\cdot\text{C}_6\text{H}_5\cdot\text{N}^-\cdot\text{N}^-\cdot\text{C}_6\text{H}_5\text{OH}
\end{align*}

The method is simple and rapid and makes use of cheap, easily available reagents which are stable and can be purchased in a high state of purity. The shade of colour produced, however, does depend upon the particular phenol present. For example, phenol itself gives a yellow dye, the mixed cresols a yellow-orange dye, the xylensols a rather deeper orange colour, and the naphthols a reddish colour. As a rule, the phenols in polluted waters, road drainage and gas liquor give a yellow-orange colour in the test and it is therefore customary in practice to use a mixture of the three cresols containing 35 per cent of the \textit{ortho} compound, 40 per cent of the \textit{meta} compound and 25 per cent of the \textit{para} compound in the preparation of standards for the colour comparison\textsuperscript{96, 300}. A B.D.H. nesslerizer disc is standardized on this mixture and covers the range 0.1-0.9 p.p.m. of cresols if a 50 ml. sample is used\textsuperscript{97, 98}.

* If a preliminary distillation is carried out, only the volatile monohydric phenols will be estimated.
A disadvantage of the method is that when some of the higher phenols are present, orange, orange-red or reddish colours may be produced and matching may be difficult unless special standards are prepared by trial from xylanols, naphthols or mixtures of these yielding a colour similar in tint to that given by the sample. The Fox-Gauge test can often be applied directly without any pre-treatment. Some samples containing interfering vegetable tannins (which contain phenolic groupings) should be pre-treated by extraction of the acidified sample with chloroform which dissolves the phenols but not the tannins; the phenols can then be recovered from the chloroform extract by shaking with aqueous sodium hydroxide. The Fox-Gauge method has been criticized on account of lack of reproducibility but satisfactory results are generally obtained if due attention is paid to certain details, namely:

1. the diazotization must be carried out in well cooled solution, preferably using ice;
2. the diazonium compound when once prepared should be used within 5–10 minutes of preparation;
3. the amount of sodium hydroxide specified in the test should be strictly adhered to, consequently samples which are acid or alkaline should be first neutralized.

In the U.S.A., the Gibbs method for the determination of phenols has achieved much popularity. The phenol is allowed to react with 2,6-dibromoquinone chloroimide in a solution buffered at pH about 9.4, when an indophenol dye is produced having in the alkaline solution a blue, green or purple colour depending on the nature of the phenol. The reaction in the case of ordinary phenol can be expressed by the equation:

\[ O: C_6H_5Br_2NCl + C_6H_2OH = O: C_6H_5Br_2N:C_6H_4OH + HCl \]

Ettinger and Ruchhoft claim to have improved the sensitivity of the method and increased the stability of the colour by extracting the coloured product with n-butyl alcohol but Riehl and Will have not reported favourably on this modification. The Gibbs method, although very sensitive, has several disadvantages. Thus, the full development of the colour takes place only when the samples have been standing at least one hour. Again, the shade of colour obtained varies with different phenols; phenol and m-cresol give a blue colour, o-cresol a purple colour, while p-cresol gives no colour at all.* Moreover, the pH must be fairly closely controlled in the

* The method therefore gives low results with gas liquors and other samples containing p-cresol.
region of pH 9·4 by buffering with borax, and any marked variation may lead to an alteration in shade. It is also essential to use a freshly prepared alcoholic solution of the reagent. Riehl and Will even state that the solid reagent deteriorates on keeping and that it is therefore advisable to purchase the compound only in small quantities at a time. Amines interfere with the method and sulphides prevent colour development.

Another method of obtaining the same indophenol dyes was worked out by Houghton and Pelly and further studied by Hill and Herndon; they produced these dyes by mixing dimethyl-p-phenylene diamine (p-aminodimethylaniline), prepared as required by reduction of p-nitrosodimethylaniline with zinc dust, with the sample buffered with sodium bicarbonate, and then oxidizing to the indophenol with sodium hypochlorite. This procedure has many of the disadvantages of the Gibbs method, and in addition suffers from other defects, such as the trouble involved in the preparation of the unstable amine, and the careful control necessary to prevent bleaching of the dye by any excess of hypochlorite. Nusbaum, however, has recently much improved and simplified this method. The troublesome preparation of the amine is avoided by using p-aminodimethylaniline oxalate, which is now available commercially and unlike the other salts of p-aminodimethylaniline is stable and does not oxidize or discolor on keeping. Sodium hypochlorite as an oxidizing agent is replaced by potassium ferricyanide which does not interfere when present in excess and also serves to oxidize any interfering sulphides. The final pH is kept at about 8·3–8·7 with a borax buffer, and the colour, after 15 minutes, is extracted with isamyl alcohol or, better, chloroform. Although amines interfere, they can be removed by shaking the sample with a strongly acidic ion-exchange resin and filtering.

Another colorimetric method for estimating phenols depends upon the interaction of phenols in alkaline solution (pH 9·6–10·0) with 4-amino-antipyrine in the presence of an oxidizing agent (potassium ferricyanide) to give an intense red coloration. In the case of phenol itself, the reaction is believed to take place as follows:
Although the method has some defects (e.g. aromatic amines react, oxidizing and reducing agents must be absent, and the intensity of the colour obtained depends upon the nature of the phenol), it has been recommended as one of the standard procedures for phenols in the latest revision of the A.P.H.A. Standard Methods.2

When relatively large amounts of phenols are present, (e.g. more than 20 p.p.m.), a volumetric method of estimation by bromination may be used:1, 15, 17;

\[
C_6H_5OH + 3Br_2 = C_6H_2Br_3OH + 3HBr
\]

The phenol is treated with excess of \(\frac{n}{10}\) bromine (\(\frac{n}{10}\) \(\text{KBrO}_3 + \text{KBr + hydrochloric acid}\)) and the unused bromine is determined by adding potassium iodide and titrating the liberated iodine with sodium thiosulphate. The results can be expressed in terms of phenol, or in terms of bromine absorbed.

**TAR BASES**

Tar bases (e.g. pyridine, quinoline, iso-quinoline and acridine) are present in coal-tar, in effluents from gas works and coke ovens, in oil refinery waste waters, and in rivers polluted by these various wastes. Tar bases are toxic to fish and tend to impart unpleasant tastes and odours to surface waters.

In the picrate method of determining moderate quantities of these bases, proposed by Fox and GAUGE, the sample is rendered alkaline with sodium hydroxide and the tar bases are extracted with chloroform. The chloroform layer is then shaken with dilute sulphuric acid when the bases pass to the upper acid layer and are isolated by making the acid slightly alkaline with sodium hydroxide and extracting with chloroform. The chloroform extract containing the tar bases is then dried with anhydrous sodium sulphate, filtered into a beaker containing a known amount of dry picric acid, evaporated slowly, dried at 70 °C and the picrates weighed.

The determination of traces of pyridine (0.005–1.0 p.p.m.) and other tar bases in polluted rivers is best carried out by the method proposed by Kroner, ETTINGER and Moore. This method is based upon the König synthesis already mentioned in connection with the Aldridge method of estimating cyanide (page 319), i.e. addition of cyanogen bromide to the pyridine or pyridine base, followed by condensation with an aromatic amine (\(\text{R} \cdot \text{NH}_2\)) in accordance with the scheme:
The aromatic amine used is benzidine, or 4:4'-diamino-diphenyl (NH₂-C₆H₄-C₆H₄-NH₂). The pyridine is first isolated from the sample by distillation and is buffered with sodium acetate to pH 6-8 and then allowed to react with cyanogen bromide and benzidine hydrochloride. The red dye so produced is extracted with butyl alcohol and estimated colorimetrically.

HYDROCARBONS

Many polynuclear hydrocarbons (e.g. naphthalene, anthracene, pyrene, 3:4-benzpyrene, etc.) occur in coal tar, in small quantities in gas works effluents, and in sewage effluents derived from sewage containing gas liquor:

- Naphthalene, C₁₀H₈
- Anthracene, C₁₄H₁₀
- Pyrene, C₁₆H₁₄
- 3:4-Benzpyrene, C₂₀H₁₂

Wedgwood, 312, 313, and Wedgwood and Cooper, 314-16A, by a combination of chromatographic and spectroscopic techniques, have developed a method of separating, identifying and estimating traces
DETECTION AND MEASUREMENT

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of polynuclear hydrocarbons in various effluents. The absorption spectra are measured by means of a Unicam spectrophotometer and compared with those of the pure hydrocarbons. Pyrene, for instance, has a very characteristic absorption peak in the ultraviolet region at a wavelength of 335 nm.

A colorimetric method of determining naphthalene in industrial wastes has been described by MEDIN and HERNDON and depends upon the blue colour produced when anhydrous aluminium chloride is added to a chloroform solution of naphthalene. The method can be used over the range 0-2-200 p.p.m. of naphthalene. Water interferes, consequently all apparatus must be carefully dried and the chloroform solution dried over anhydrous alumina. Phenols and anthracene do not interfere but sulphides must be removed with silver nitrate and sodium hydroxide.

SYNTHETIC INSECTICIDES

Numerous synthetic insecticides are now known (cf. page 84) and are toxic in very small concentrations not only to insects but also to fish. Sensitive methods for the estimation of traces of these compounds are therefore much needed. The most widely known of the newer insecticides are DDT and the y-isomer of benzene hexachloride (page 85). These two insecticides have been used at sewage filter installations for controlling and destroying certain flies (especially the species Psychoda and Anisopus) which are such a nuisance during the warmer months of the year (cf. page 435).

BERCK has described a colorimetric method suitable for the determination of concentrations of DDT as low as 0·003 p.p.m. in river water and suspended solids. It is based upon the Schechter-Haller method in which the DDT, after preliminary isolation by extraction with a mixture of ether and n-hexane, is nitrated to a polynitro derivative, a benzene solution of which gives an intense blue colour with sodium methoxide dissolved in methyl alcohol. It is to be noted that solids suspended in streams, such as clay, silt, and very fine sand, can easily adsorb DDT.

A method for the estimation of traces of the y-isomer of benzene hexachloride (‘gammexane’) has been described by SCHUCHTER and HORNSTEIN. The water or effluent is first extracted with carbon tetrachloride to dissolve the insecticide and the extract is evaporated at as low a temperature as possible to remove the solvent. The benzene hexachloride is then dechlorinated to benzene by treatment with zinc and acetic acid and the benzene is absorbed in a mixture of nitric and sulphuric acids. The m-dinitrobenzene so formed is allowed to react with methyl ethyl ketone and alkali to give a reddish-violet coloration, the intensity of which is measured.
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photometrically. The various chemical reactions must be performed in a special all-glass apparatus. As little as 0·005 mg of the insecticide can be estimated by this method. HANCOCK and LAWS isolate benzene hexachloride from large volumes of effluents by adsorption on purified activated charcoal; the insecticide is then determined by a modified Schechter–Hornstein procedure using a simplified dechlorination and nitration apparatus. Other common chlorinated insecticides cause no interference with the method but aromatic hydrocarbons (e.g. benzene, toluene and xylene) interfere. In the presence of these hydrocarbons, the determinations are carried out with and without addition of zinc to enable a correction to be applied.

SYNTHETIC DETERGENTS

The presence of small amounts of synthetic detergents in sewage effluents, trade wastes and river waters, the objectionable tendency of these detergents to cause persistent foam on streams and at sewage plants, and the toxicity of these detergents towards fish and aquatic flora, make it very important to find suitable methods for their estimation.

The most widely used methods in this country for determining small amounts of anionic synthetic detergents are based upon the formation of a chloroform-soluble blue complex of methylene blue and the detergent (see references 322–7). The committee on synthetic detergents set up by the Ministry of Housing and Local Government has now suggested that determinations of anionic synthetic detergents in sewage and river waters should be carried out by a standard procedure recommended by the Government Chemist’s department and described in a recent issue of the Analyst. This method, whilst utilizing the formation of the blue complex of methylene blue and the detergent, differs from previously published methods in carrying out the extraction of the complex with chloroform in an alkaline solution (phosphate-sodium hydroxide buffer at pH 10) instead of an acid medium. The chloroform extracts are eventually washed with an acid solution of methylene blue. By using this double extraction procedure, interference due to chloride, nitrate, thiocyanate and proteins, to which previous methods were subject in varying degree, is reduced to negligible amounts. The colour intensity of the chloroform extract is measured absorptionmetrically using an orange filter at 650 mμ. The anionic detergent sodium dioctylsulphosuccinate (‘Manoxol O.T.’), which can be purchased in a high state of purity and is stable both in the solid state and in aqueous solution, is recommended as a reference standard for the preparation of the calibration curve.
DETECTION AND MEASUREMENT

Sulphides interfere with the method by reducing the methylene blue but they can be removed by a preliminary oxidation with hydrogen peroxide. If a distinction between sulphate detergents (e.g. Teepol) and sulphonate detergents (e.g. Tide) is desired, the procedure described by DEGINS and his associates can be adopted. The combined anionic detergents (sulphate + sulphonate) are first determined; the concentration of sulphonate detergents is then determined on another portion of the sample after the sulphate detergents have been hydrolysed by boiling with sulphuric acid. The difference between the two determinations gives the concentration of sulphate detergents.

Anionic synthetic detergents can also be determined by titration methods. EDWARDS and GINN have described a modified titration method for determining anionic detergents in sewage based upon the original two-phase titration procedure of BARR, OLIVER and STUBBINGS. The titration is carried out with a standard solution of the cationic detergent, cetyl trimethylammonium bromide, in the presence of hexane, a solution of bromophenol blue or azophloxine being used as indicator. The dyestuff forms a coloured salt with the slightest excess of cationic detergent, thus indicating the end-point by the colour imparted to the hexane layer. Interference by proteins and soaps is prevented by buffering between pH 7.0 and 7.5, and interference due to hardness by adding the di-sodium salt of ethylene diamine tetra-acetic acid (EDTA). The results are unaffected by thiocyanates, nitrates, or urine, and there is no interference by sodium chloride or sodium sulphate in concentrations up to about 1000 p.p.m.

On the basis of the experiments of SCHAFFER and CRITCHFIELD and HEATLEY and PAGE, Imperial Chemical Industries, Ltd., have developed a routine method for estimating non-ionic detergents of the polyethanoxy type (e.g. Lissapol N) present in concentrations of about 2–20 p.p.m. of active agent. Practical details of the method are available from the Ministry of Housing and Local Government. The method depends upon the extraction of the non-ionic detergent with ether in the presence of salt and the formation of an insoluble complex compound of the detergent with barium phosphomolybdate in hydrochloric acid–ethanol solution. This complex is digested with a mixture of sulphuric and perchloric acids and the phosphate so formed, which is a measure of the amount of detergent present, is estimated colorimetrically by reduction to molybdenum blue according to the TSCHOPP procedure, i.e. using sodium metabisulphite in the presence of sodium sulphite and metol. The results are reproducible to within ±2 p.p.m. The method is suitable for satisfactory sewage effluents and probably also for reasonably clean river waters, but for polluted samples...
ASPECTS OF RIVER POLLUTION

(e.g. sewage) a preliminary deproteinization with zinc sulphate and barium hydroxide is necessary as a rule. The method, although rather lengthy, is the only routine one at present available.

FATS AND GREASE

The estimation of fatty and greasy matter in sludges, effluents and polluted river waters is usually carried out by extraction of the sample with an organic solvent followed by the evaporation of the extract and the weighing of the dried residue. Numerous organic solvents have been recommended in the past for this estimation, especially light petroleum, hexane, diethyl ether, benzene, and chloroform. Since the amount of lipoidal matter extracted depends upon the particular solvent selected, it is important that the name of the solvent used should always be specified.

KNECHTGES, PETERSON and STRONG investigated petroleum, ethyl ether, isopropyl ether and chloroform as solvents for the extraction of greasy material from samples of sludge from six different sewage plants and found that chloroform extracts the largest quantity of fatty matter and light petroleum the smallest amount; chloroform extracting about twice as much lipoidal material as did petroleum. Metallic soaps are more easily soluble in chloroform than in petroleum but even when the sludge was acidified to hydrolyse these soaps to fatty acids, petroleum still extracted less material than did chloroform without acidification. Similar results have been reported by other workers. KNECHTGES, PETERSON and STRONG investigated petroleum, ethyl ether, isopropyl ether and chloroform as solvents for the extraction of greasy material from samples of sludge from six different sewage plants and found that chloroform extracts the largest quantity of fatty matter and light petroleum the smallest amount; chloroform extracting about twice as much lipoidal material as did petroleum. Metallic soaps are more easily soluble in chloroform than in petroleum but even when the sludge was acidified to hydrolyse these soaps to fatty acids, petroleum still extracted less material than did chloroform without acidification. Similar results have been reported by other workers. However, has found that when samples of sewage sludge are digested with acid, filtered, washed with water and dried, the amounts of greasy matter extracted from the dried residue by light petroleum, carbon disulphide, ethyl ether, and chloroform are not significantly different. GEHM and TRUBINICK have given several reasons for preferring, in general, petroleum as a grease solvent for sewage sludges. POMEROY and WAREMAN in a comprehensive study of numerous grease solvents concluded that petroleum or hexane tended to dissolve material which more nearly resembled the grease contained in sewage, sludge, and trade wastes. In the U.S.A., light petroleum has been recommended as the standard grease solvent and acidification is always adopted as a pre-treatment procedure in order to hydrolyse metallic soaps to fatty acids. In the A.P.H.A. Standard Methods grease is officially defined as 'that material which is extracted from an acidified sample of sewage or sludge' by petroleum ether (boiling range 35–54°C) when using the standard method.

STEPHENSON has reported that the drying of acidified sewage
DETECTION AND MEASUREMENT

sludges by heat leads to low grease results, and has suggested a shorter more accurate procedure for grease determination than that recommended in the U.S.A. It involves dehydrating the liquid sludge (which has been previously acidified with hydrochloric acid) by stirring with magnesium sulphate monohydrate for about 15-30 minutes and extracting the ground product with light petroleum for five hours in a Soxhlet apparatus.

It is sometimes desirable to ascertain the nature of the fatty material extracted from a sample. For example, it is often important to know the proportion of unsaponifiable matter present, i.e. sterols, hydrocarbons and mineral oils (e.g. motor oils) not volatile at 100°C. This determination is generally carried out by saponifying the vegetable and animal fats with boiling alcoholic potash and then extracting the unsaponifiable material with light petroleum or ethyl ether. Gehm and Trubnick have found that boiling aqueous 10 per cent sodium hydroxide is just as satisfactory as the alcoholic alkali for this saponification, and much more convenient to use.

OTHER CHEMICAL METHODS

A selected list of methods for the determination of additional substances occasionally encountered in sewage, trade wastes and river waters is given in outline in Table 58.

Table 58. Methods for the determination of some additional substances occasionally found in sewage, trade wastes and river waters

<table>
<thead>
<tr>
<th>Substance, element, or material</th>
<th>Occurrence</th>
<th>Method of determination</th>
<th>Usful range of</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetylene</td>
<td>Lime wastes from acetylene generators</td>
<td>Reaction with ammonia-0.01N silver nitrate to give insoluble silver acetylde and titration of acidified filtrate with 0.01N ammonium thiocyanate</td>
<td>—</td>
<td>7</td>
</tr>
<tr>
<td>Aluminium</td>
<td>—</td>
<td>Colorimetric, with Haematoxylin</td>
<td>0.1-0.5 p.p.m.</td>
<td>4, 98</td>
</tr>
<tr>
<td>Boron</td>
<td>pH adjusted to 7-6, mannitol (3 g per 100 ml.) is added, and the liquid is titrated back to pH 7-6 with standard caustic soda</td>
<td>—</td>
<td>343</td>
<td></td>
</tr>
</tbody>
</table>
### Table 58-ant.

<table>
<thead>
<tr>
<th>Substance, element, or material</th>
<th>Occurrence</th>
<th>Method of determination</th>
<th>Useful range of method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Bromide</strong></td>
<td>Sea-water (about 65-70 p.p.m. of Br)</td>
<td>Oxidation by chlorine water to bromate. After removing excess of chlorine with sodium formate, the bromate is determined iodometrically by adding a few drops of ammonium molybdate solution (catalyst), potassium iodide, and hydrochloric acid and titrating the liberated iodine with 0.001N thiosulphate. Organic matter should be destroyed by evaporation of the sample and gentle ignition.</td>
<td>0.05-2.5 p.p.m. (25-1,000 ml sample)</td>
<td>344</td>
</tr>
<tr>
<td><strong>Glucose</strong></td>
<td>—</td>
<td>Sample heated with alkaline potassium ferricyanide. The ferrocyanide so formed is estimated by acidification and titration with 0.01N ceric sulphate using Setopaline C as indicator.</td>
<td>—</td>
<td>345</td>
</tr>
<tr>
<td><strong>Lactose</strong></td>
<td>Dairy wastes</td>
<td>After removal of proteins with sulphuric acid and sodium tungstate, alkaline copper tartrate and sodium bisulphite are added, and the cuprous copper so formed is allowed to reduce phosphomolybdic acid to molybdenum blue, which is determined absorptiometrically.</td>
<td>0.5-5.000 p.p.m.</td>
<td>346</td>
</tr>
<tr>
<td><strong>Magnesium</strong></td>
<td>Sea-water (about 1,400 p.p.m.)</td>
<td>(a) Gravimetric, as Mg₂PO₄</td>
<td>—</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Estuary water</td>
<td>(b) Colorimetric, with Titan yellow</td>
<td>0.1-4.0 p.p.m.</td>
<td>2, 98, 222</td>
</tr>
<tr>
<td></td>
<td>—</td>
<td>(c) Titrmetric, with EDTA</td>
<td></td>
<td>See page 296</td>
</tr>
<tr>
<td><strong>Phosphate</strong></td>
<td>—</td>
<td>Reduction of phosphomolybdate to molybdenum blue with stannous chloride</td>
<td>0.05-0.5 p.p.m. of PO₄</td>
<td>1, 4, 98</td>
</tr>
</tbody>
</table>
DETECTION AND MEASUREMENT

Table 58—cont.

<table>
<thead>
<tr>
<th>Substance</th>
<th>Occurrence</th>
<th>Method of determination</th>
<th>Useful range of method</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silica</td>
<td>—</td>
<td>Colorimetric, as yellow silico-molybdate, oxalic acid being added to destroy colour due to phosphate</td>
<td>1-20 p.p.m.</td>
<td>2, 4, 12, 96</td>
</tr>
<tr>
<td>Sugars</td>
<td>Citrus wastes, sulphite cellulose wastes, beet sugar wastes</td>
<td>Converted to reducing sugars by acid hydrolysis, then heated with alkaline potassium ferri cyanide. The excess of ferricyanide is determined iodometrically</td>
<td>—</td>
<td>347</td>
</tr>
<tr>
<td>Trichloroethylene*</td>
<td>—</td>
<td>Sample + pyridine + caustic soda—orange colour when heated for 5 minutes in boiling water bath</td>
<td>1-20 p.p.m.</td>
<td>348</td>
</tr>
</tbody>
</table>

* Carbon tetrachloride and chloroform give a similar colour reaction.

BACTERIOLOGICAL METHODS

The physical and chemical examinations generally carried out in the laboratories of water works, sewage disposal works, and river boards, all follow a rather similar pattern, but the application of bacteriology is somewhat different in both extent and purpose in each case. The statutory duties of these three authorities provide a lead as to the manner in which bacteriology should be applied.

In the case of the water works, under obligation to provide a pure and wholesome water at all times, the bacteriological examination for indicators of possible pathogenic contamination, namely the organisms of intestinal origin, must be carried out frequently in order to ensure that the water entering the distribution system complies with the recommendations regarding the coliform count laid down in the Ministry of Health Report in this country (see also Chapter 5, page 98). In the U.S.A. similar recommendations are laid down in the Public Health Reports of the U.S. Public Health Service.

The sewage works, whose task is to purify water after use, is not usually interested in the detection of any particular bacterium or group of organisms, and indeed, the effluent from a well-purified sewage treated by the activated sludge process or by percolating filters will normally contain many thousands of bacteria (see...
Chapter 6, page 132, and Chapter 12, page 450). The sewage works laboratory is more concerned with the extent of purification brought about by bacteria and other organisms in the treatment plant. Fortunately, nowadays, the presence of pathogens of the enteric type in sewage is extremely rare in this country owing to the progress made in sanitary science but may constitute a hazard in other countries, especially in tropical and semi-tropical regions. If the presence of pathogenic organisms is suspected, then an examination for them should be made. The only organism which is likely to be a menace in this country today is *Salmonella typhi* and Moore's swab method is available for its detection in sewage.

The river board is also more concerned with the changes brought about by bacteria rather than with the detection of any particular bacterium or group of bacteria. In this connection, it is important to remember that the ultimate disposal of sewage takes place by dilution, usually in rivers, and it is this fact which provides the key to the bacteriological work of the river board. Trade wastes, usually after treatment, also discharge into rivers as a rule, and if a discharge contains substances which are toxic to bacteria, the aerobic decomposition of organic wastes in the stream will be retarded or even completely inhibited, i.e. there will be a repression of normal self-purification. When this repression is due to inhibitory substances as opposed to unduly heavy loads of organic matter or to the presence of an oily scum which hinders re-aeration, then the results of a chemical analysis of the river water can be misleading. In particular, the tests likely to be unreliable on account of repression of bacterial metabolism are set out in Table 59.

*Table 59. Chemical tests influenced by repression of bacterial activity in river water due to presence of toxic substances*

<table>
<thead>
<tr>
<th>Test</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved oxygen</td>
<td>May be high due to low requirements of the few bacteria present</td>
</tr>
<tr>
<td>B.O.D.</td>
<td>May be low due to little or no attack on the organic matter by the few aerobic bacteria present</td>
</tr>
<tr>
<td>Free ammonia (ammoniacal nitrogen)</td>
<td>May be low since completion of breakdown of nitrogenous organic matter will be delayed</td>
</tr>
<tr>
<td>Stability test</td>
<td>Unreliable due to dependence on bacterial activity</td>
</tr>
</tbody>
</table>

In such circumstances, only the 4 hours permanganate value and the figure for albuminoid (or organic) nitrogen will provide an indication of the organic load in a river. In a circular issued in
In 1954 by the Ministry of Housing and Local Government, the following occurs on the subject of 'Repression of natural self-purification processes':

'It may be important to determine whether effluents reduce the rate of self-purification of river waters and some control of this property may be desirable. At present, however, no suitable test is in existence.'

The desired test might well be a bacteriological procedure, perhaps on the lines of the Rideal-Walker test for evaluating the potency of disinfectants. In this test, *Salmonella typhi* (formerly called *B. typhosa*) is used as the test organism and phenol as the reference standard. The result is expressed as the 'Phenol Coefficient', i.e. the number calculated by dividing the denominator of the fraction expressing the greatest dilution of the disinfectant required to kill the organism in 10 minutes (but not 5 minutes) by the corresponding figure for the greatest phenol dilution showing the same results. When investigating the effects of inhibitory trade wastes, an inorganic toxic substance might prove more suitable than phenol as a reference standard since phenol can serve as a bacterial food when sufficiently diluted.

Bacteriological methods can also be used in river pollution studies for the detection of certain types of pollution where chemical methods fail. Chemical analysis may indicate that nitrogenous organic matter is present but a test for the presence of faecal organisms is necessary to establish whether the discharge contains sewage or arises from an industrial process. In view of the widespread distribution of the coliform group of organisms generally used as indicators, it is advisable to perform differential tests to decide whether the majority of the organisms consist of *Escherichia coli* (the more usually accepted intestinal organism) or whether the intermediate and aerogenes-cloacae groups predominate (i.e. those more usually associated with soil and vegetation). There are, unfortunately, no reliable methods for distinguishing between faecal organisms of human and animal origin and consequently no reliable means of detecting whether sewage or farm drainage is present.

There is one aspect of pollution detection in which it has been shown that a bacteriological examination gives useful results, namely the examination of the muds of polluted lakes and estuaries. A paper by Allen, Grindley and Brooks makes it clear that chemical analysis alone will not indicate satisfactorily whether a mud has been deposited with faecal matter or with other organic matter in the distant past. These authors showed that counts of coliform organisms and of *Streptococcus faecalis* in the surface layers...
of the mud can indicate whether faecal pollution has taken place during the deposition of the mud.

The normal disappearance of bacteria from a stream, as a polluting discharge of sewage or trade waste is carried downstream, can be determined by a sanitary survey. It is considered advisable to employ a more exact method for the enumeration of bacteria at various points along the river than is afforded by determinations of 'Most Probable Numbers' used for potable waters. For this purpose, a modification of colony counting for polluted waters has been put forward by Allen, who uses the more reliable thermos-tatically-controlled water bath rather than the customary incubator whose temperature is difficult to control accurately. The inoculum and the agar are distributed over the inside of a closed bottle by spinning the bottle rapidly after adding the contents. Apart from this 'spinning bottle technique', Allen recommends that if the method of 'Most Probable Numbers' be employed, then a 'Resuscitation Procedure' should be used in which the inoculum of water is incubated for a short time in the sugar broth to revive old bacterial cells or those weakened by long immersion in water. The selective agent is then added, namely bile salts for E. coli and sodium azide for St. faecalis.

Regarding practical aspects of bacteriological technique, it may be noted that there are important differences in the composition of the media used in English and American practice. The use of 'molecular filter membranes' (discs of cellulose esters having a uniform pore size) for removing bacteria quantitatively from samples, is gaining ground as a new technique in the bacteriological examination of waters and has many advantages over the classical methods.

BIOLOGICAL METHODS

USE OF BIOLOGICAL INDICES OF POLLUTION

The use of aquatic plants and aquatic animals for the detection and assessment of pollution has received much attention in recent years and is based upon the differential or sometimes complete elimination of certain species by specific pollutants. Much useful information can be obtained by comparing the numbers and kinds of flora and fauna well above a source of pollution with those inhabiting the stream below the pollution. The types of life present may also vary with the nature of the stream bed, i.e. whether mud or gravel.

In general, it can be stated that where organic pollution is high,
very few, if any, diatoms, protozoa or algae will be found but there will be greyish slimy masses of filamentous organisms ('sewage fungus') and colourless plants requiring organic matter for their nutrition as well as such dirty water organisms as the mud-inhabiting worms, such as tubificids and Chironomus larvae ('blood-worms'). Such organisms as Asellus (the common water-louse) and leeches usually favour moderately polluted waters or waters recovering from organic pollution. Where pollution is negligible, and the water is reasonably clean and well aerated, larvae of the stone-fly, may-fly and caddis-fly are to be found as well as green water plants such as water moss, pondweed (Potamogeton) and water buttercup; green algae and diatoms are present, mould-fungi are absent and such animals as Gammarus (the freshwater shrimp) and water-snails may be conspicuous. Further details on the use of aquatic flora and fauna as indicators of pollution are given in Chapter 8.

The importance of conducting biological surveys lies in the fact that valuable information may be obtained about stream conditions that have existed long before the survey has been carried out. Chemical and physical data on the other hand only reflect the state of the stream at the actual time of sampling and so may not always give the desired information about intermittent pollutions. The results of a biological survey are, however, sometimes difficult to interpret even when the services of an experienced biologist are available. Moreover, although a biological investigation may reveal that an accidental or intermittent pollution has occurred, only a chemical examination can determine the nature and amount of the substance or substances causing pollution.

**FISH TOXICITY TESTS**

The approximate estimation of the toxicity of poisons towards fish from survival time-concentration curves obtained from laboratory tests on various dilutions of the toxic substance has already been discussed in Chapter 7. With many poisons there is an approximately linear relationship between the logarithm of the period of survival and the logarithm of the concentration of the poison. The reader may be reminded here of the many difficulties attending such experiments and of the many variables which may influence the results. Of particular importance in this connection are variations in the results obtained due to the particular species of fish used; its age, size, state of health and degree of acclimatization; the temperature; the duration of the test; the chemical composition of the water, especially the dissolved oxygen content, the pH value, the dissolved mineral salts, and the hardness. Different species of fish
vary considerably in their reaction to a particular poison, goldfish, for example, being rather more resistant to toxic substances than trout. In the interpretation of the results of laboratory toxicity tests, it must be remembered that conditions are unlikely to be the same as in the river where the water may be quite different in composition from the water used in the experiments. Moreover, some poisons may increase or reduce the toxicity of others.

A convenient and useful practical method of assessing the effect of industrial wastes or discharges on fish in a river is to observe the mortality or cases of distress amongst fish confined in cages, boxes or traps in specified positions in the river, when results are sometimes obtained in a comparatively short time. Since fish so confined cannot take any avoiding action, the results must be interpreted with caution and may not be the same as those obtained under normal conditions in the stream. Moreover, although fish might survive in a cage, this does not necessarily imply that they would thrive and breed happily under ordinary stream conditions.

For experimental details of carrying out laboratory toxicity tests and for descriptions of various species of fish and particulars of their care and management, the reader is referred to the literature on the subject (see references 367-77).

Unfortunately, a really simple straightforward toxicity test suitable for routine work has not yet been devised. The Ministry of Agriculture, Fisheries and Food in conjunction with the Water Pollution Research Laboratory and the Freshwater Biological Association are carrying out a research programme on the effect of various poisons on fish. It is hoped that eventually a standard procedure for determining toxicity will be developed as a result of this work, and it will then be possible for the Ministry to examine effluents for toxicity in a special laboratory to be set up in London.

Data showing the lethal limits to fish of some important pollutants have been given previously (see Chapter 7, Table 35). More extensive data are to be found in the comprehensive literature survey published by the California State Water Pollution Control Board 378.

USE OF DAPHNIDS AND OTHER LOWER ANIMALS FOR TOXICITY TESTS

Since crustacea and other lower aquatic animals serve as sources of food for fish, it is obviously of importance to determine the effect on these organisms of various toxic and other substances found in trade wastes. Experiments along these lines using the crustacean *Daphnia magna* (the common water-flea) as test animal have been carried out by Anderson 379-81, who determined the threshold concentration for the immobilization (i.e. cessation of swimming
movements) of this organism by various substances when added to Lake Erie water at 25° C. These threshold concentrations (i.e. the highest concentration just failing to immobilize 50 per cent of the animals under prolonged exposure) were estimated graphically from immobilization time–concentration curves. Anderson has pointed out that the use of Daphnia as an experimental animal for these tests has many advantages, such as:

(a) the ease of culture of these animals,
(b) their small size (up to 5 mm),
(c) their comparatively short life span (up to about 2 months at 25° C), and
(d) the fact that they mature so quickly that they can produce offspring during the first week of life.

Some results obtained by Anderson are given in Table 60.

Table 60. Threshold concentrations for the immobilization of Daphnia magna by various substances when added to Lake Erie water at 25° C. (After Anderson.)

<table>
<thead>
<tr>
<th>Substance</th>
<th>Threshold concentration p.p.m.</th>
<th>Substance</th>
<th>Threshold concentration p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>150</td>
<td>Silver nitrate</td>
<td>0.0055</td>
</tr>
<tr>
<td>Aluminium sulphate</td>
<td>136</td>
<td>Sodium arsenite</td>
<td>9.1</td>
</tr>
<tr>
<td>[Al(OctO)4]</td>
<td></td>
<td>Sodium monomethylene arsenate (Na2H2AsO4)</td>
<td>20</td>
</tr>
<tr>
<td>Ammonium chloride</td>
<td>91</td>
<td>Sodium hydrogen</td>
<td>2.0</td>
</tr>
<tr>
<td>Ammonium hydroxide</td>
<td>&lt;0.75</td>
<td>Sodium bicarbonate</td>
<td>2.350</td>
</tr>
<tr>
<td>Ammonium sulphate</td>
<td>&lt;0.10</td>
<td>Sodium carbonate</td>
<td>&lt;0.02*</td>
</tr>
<tr>
<td>Barium chloride (BaCl2)</td>
<td>29</td>
<td>Sodium cyanide</td>
<td>4.242</td>
</tr>
<tr>
<td>Cadmium chloride</td>
<td>&lt;0.0026</td>
<td>Sodium hydroxide</td>
<td>&lt;3.4</td>
</tr>
<tr>
<td>Calcium chloride (CaCl2)</td>
<td>920</td>
<td>Sodium fluoride</td>
<td>3.04</td>
</tr>
<tr>
<td>Chronic acid (CrO3)</td>
<td>&lt;0.6</td>
<td>Sodium hydroxide</td>
<td>1.56</td>
</tr>
<tr>
<td>Chronic chloride (CrCl3)</td>
<td>&lt;0.06</td>
<td>Sodium nitrate</td>
<td>5.000</td>
</tr>
<tr>
<td>Cupric chloride (CuCl2)</td>
<td>&lt;0.01</td>
<td>Sodium nitrate</td>
<td>&lt;0.20</td>
</tr>
<tr>
<td>Cupric sulphate (CuSO4)</td>
<td>&lt;0.01</td>
<td>Sodium sulphate</td>
<td>0.006</td>
</tr>
<tr>
<td>Ferric chloride (FeCl3)</td>
<td>130</td>
<td>Sodium sulphate (Na2S)</td>
<td>5.960</td>
</tr>
<tr>
<td>Ferric sulphate (Fe2SO4)</td>
<td>&lt;0.15</td>
<td>Sodium sulphate (Na2S)</td>
<td>9.4</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>62</td>
<td>Sodium sulphate (Na2S2O3)</td>
<td>440</td>
</tr>
<tr>
<td>Merecuric chloride</td>
<td>&lt;0.006</td>
<td>Sodium thiosulphate</td>
<td>&lt;11.3</td>
</tr>
<tr>
<td>Nickel chloride (NiCl2)</td>
<td>&lt;0.7</td>
<td>Sulphuric acid</td>
<td>88</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>107</td>
<td>Tannic acid</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Phenol (C6H5OH)</td>
<td>94</td>
<td>Zinc chloride (ZnCl2)</td>
<td>&lt;0.15</td>
</tr>
<tr>
<td>Potassium dichromate</td>
<td>&lt;0.06</td>
<td>Zinc sulphate (ZnSO4)</td>
<td>&lt;0.48</td>
</tr>
<tr>
<td>Potassium permanganate</td>
<td>0.65</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Corresponding to about 0.1 p.p.m. of Cr.
It should be emphasized that these results apply to Lake Erie water and consequently may be different if other waters differing in hardness and composition from Lake Erie water are used.

**USE OF BIOLOGICAL METHODS FOR DETERMINING TRACES OF METALS OR OTHER CHEMICAL SUBSTANCES**

Fungi have been used for determining minute traces of metals (e.g. iron, copper, zinc, molybdenum and manganese) in such biological materials as soils, the ash of plants and fruit extracts. In principle, the bio-assay method depends upon the fact that fungi such as *Aspergillus niger* and *Penicillium glaucum* require for optimum growth such micro-nutrients as iron, copper, zinc, molybdenum and manganese. Hence, by adding known and graded quantities of the micro-nutrient to be estimated to a culture solution containing all the other essential nutrients, increased growth of the particular fungus takes place which can be assessed by determining the weight of mycelium and the nature of the spore cover. According to Nicholas, the smallest amounts of metals that can be detected by this bio-assay procedure (in microgrammes of metal per 50 ml. of culture solution) are as follows: copper, 0.05; zinc, 0.25; iron, 0.01; manganese, 0.01; molybdenum, 0.0001. These are, in general, far below the amounts that can be estimated by chemical methods but the procedure has not yet been applied to the detection of metallic contaminants in trade wastes or river waters.

A somewhat analogous method, involving the inhibition of the growth of *Mucor spinosus*, has been employed to estimate small quantities of organic mercury compounds used in paper making to prevent slime growths; the extent to which germination is inhibited is compared with the extent of inhibition in a series of standard cultures containing known amounts of the organic mercury compound.

Tomlinson and his co-workers have described an ingenious and comparatively simple biological method of estimating the concentration of the gamma-isomer of benzene hexachloride ('gammexane') in sewage effluents. The method is based upon the curious property possessed by this insecticide, when present in concentrations greater than about 0.005 p.p.m., of inhibiting the formation by *Chironomus larvae* ('blood-worms') of tubes from activated sludge. Hence, in order to determine the concentration of gammexane in a sample, activated sludge is supplied to the larvae in a series of dilutions of the sample and the presence or absence of tubes is noted.
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CHAPTER 10

SIGNIFICANCE AND INTERPRETATION OF CHEMICAL TESTS

Nearly all the grandest discoveries of science have been the rewards of accurate measurement and patient long-continued labour in the minute sift of numerical results.

LORD KELVIN.
Address to the British Association, 1871

In this chapter, an attempt will be made to assess the significance of some of the chemical tests used in river survey work. The correct interpretation of the results of a chemical analysis is by no means an easy matter. In general, each test should be considered not in isolation but in relation to the analysis as a whole. Moreover, it is often difficult to interpret chemical analyses fairly unless they are supplemented by bacteriological and biological surveys, by observations on stream flows and rainfall, by data on the volume and frequency of the discharges to the stream and by other relevant information on the local conditions prevailing.

DISSOLVED OXYGEN

The concentration of dissolved oxygen is one of the most important indices of the purity of a stream, and one of the first indications of the presence of organic pollution is a fall in the dissolved oxygen content of the stream below the source of the pollution. Since the deoxygenation of water by sewage and trade wastes is a comparatively slow process, the point of maximum deoxygenation may be anything up to several miles downstream of the point of pollution.

The amount of oxygen taken up by water from the atmosphere is dependent on the temperature, the barometric pressure, and the amount of chloride in the water. Solubility of oxygen falls markedly with rise in temperature and increases with a rise in pressure, and is rather less in water containing chloride than in fresh water; thus, the amount of oxygen dissolved by sea water (containing 20,000 p.p.m. of chloride, expressed as Cl) in equilibrium with air is only about 80 per cent of that taken up by fresh water.

The figures generally used for the solubility of oxygen in fresh and salt water are those given by the American Public Health Association and were calculated by Whipple and Whipple from
gasometric determinations carried out by Fox as early as 1909. Investigations at the Water Pollution Research Laboratory by Truesdale, Downing and Lowden, however, have shown that the correct values determined by a modification of the standard Winkler method are lower than the generally accepted values, the error in some cases being as much as 3-4 per cent. According to these workers, the solubility of oxygen can be represented by the empirical equation:

\[ C_s = 14.161 - 0.3943T + 0.007714T^2 - 0.0000646T^3 \]

where \( C_s \) = saturation concentration of oxygen in p.p.m. and \( T \) = temperature in degrees centigrade.

Data based on this recent work for the solubility of oxygen in water in equilibrium with air at various temperatures, and salinities under a pressure of 760 mm, are given in Table 107 in the Appendix.

As an example, it will be seen from the table that if the river temperature is 13°C the amount of dissolved oxygen present is 10.2 p.p.m. and this would represent 100 per cent of saturation. A lower figure than this (e.g. 5.1 p.p.m. = 50 per cent of saturation at 13°C) would probably indicate the presence of organic pollution whilst a figure greater than 100 per cent would indicate that active photosynthesis (page 134) was taking place.

The values given in the table do not represent the solubility of pure oxygen in water which is very much higher. Air contains only 20.9 per cent of oxygen, the rest being mainly nitrogen. When air is dissolved in water, the amounts of oxygen and nitrogen dissolved depend upon the partial pressure (Henry’s law) and solubility of each gas (oxygen is about twice as soluble in water as nitrogen). At 14°C water saturated with air contains about 10 p.p.m. of oxygen but the solubility of pure oxygen at that temperature is about 48 p.p.m. or nearly five times as much. It is, therefore not surprising that figures exceeding 100 per cent of saturation are sometimes obtained in river waters particularly when photosynthesis is proceeding.

The Royal Commission on Sewage Disposal considered that the dissolved oxygen content of a river should not fall below about 60 per cent of saturation in the summer if nuisance was to be avoided, but it is generally considered nowadays that this gives a fairly wide margin of safety. In relatively unpolluted streams, the water is often supersaturated with dissolved oxygen, i.e. values exceeding 100 per cent of saturation are obtained. As already explained this is due to photosynthesis, whereby plants (especially the green and blue-green algae) under the influence of sunlight convert carbon dioxide into oxygen (page 134). Owing to photosynthesis the dissolved oxygen content of a clean stream may vary considerably
during the day and will generally be higher than at night, higher on a sunny day than on a relatively dull day and much higher on bright summer days than on dull winter days. The effect of sunshine on the hourly variation of dissolved oxygen in a river is well illustrated by data obtained by Mohlman and his co-workers for the Illinois river and quoted by Schroepfer. These are shown in Table 61.

**Table 61. Effect of sunshine on hourly variation of dissolved oxygen on two consecutive days in August 1927, in Illinois river at Averysville, Illinois**

<table>
<thead>
<tr>
<th>Time</th>
<th>Dissolved oxygen: per cent of average</th>
<th>25 August 1927</th>
<th>26 August 1927</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40% possible sunshine</td>
<td>99% possible sunshine</td>
</tr>
<tr>
<td>12 midnight</td>
<td></td>
<td>100</td>
<td>87</td>
</tr>
<tr>
<td>2 a.m.</td>
<td></td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>4 a.m.</td>
<td></td>
<td>87</td>
<td>77</td>
</tr>
<tr>
<td>6 a.m.</td>
<td></td>
<td>86</td>
<td>75</td>
</tr>
<tr>
<td>8 a.m.</td>
<td></td>
<td>96</td>
<td>83</td>
</tr>
<tr>
<td>10 a.m.</td>
<td></td>
<td>96</td>
<td>78</td>
</tr>
<tr>
<td>12 noon</td>
<td></td>
<td>98</td>
<td>92</td>
</tr>
<tr>
<td>2 p.m.</td>
<td></td>
<td>107</td>
<td>119</td>
</tr>
<tr>
<td>4 p.m.</td>
<td></td>
<td>111</td>
<td>139</td>
</tr>
<tr>
<td>6 p.m.</td>
<td></td>
<td>111</td>
<td>133</td>
</tr>
<tr>
<td>8 p.m.</td>
<td></td>
<td>108</td>
<td>122</td>
</tr>
<tr>
<td>10 p.m.</td>
<td></td>
<td>101</td>
<td>114</td>
</tr>
<tr>
<td>Average dissolved oxygen: p.p.m.</td>
<td></td>
<td>6.92</td>
<td>8.65</td>
</tr>
</tbody>
</table>

The data in the table show that

(a) The maximum concentration of dissolved oxygen was 139 per cent of the average on the very sunny day but only 111 per cent of the average on the duller day. In actual amounts of dissolved oxygen, this would be 12.0 p.p.m. on the sunny day but only 7.7 p.p.m. on the dull day.

(b) The average dissolved oxygen content was considerably higher on the sunny day than on the preceding dull day.

(c) The highest concentration of dissolved oxygen occurs during the afternoon (2-6 p.m.) on each day.

Schroepfer has presented data showing that rivers having a low average concentration of dissolved oxygen show more hourly variation than those having a higher concentration of dissolved oxygen. Consequently, owing to the variations in dissolved oxygen from hour to hour, the taking of 'snap' samples can give misleading results. Obviously a sample for dissolved oxygen determination should be taken at a time when the oxygen content is as near the average as possible. Analysis of data on the Mississippi river showed
that samples collected between sunset and midnight generally gave dissolved oxygen values nearer the average for the day, but in practice sampling would be inconvenient so late in the day and so Schroepfer suggests a time between 7 a.m. and 12 noon. Alternatively, the use of automatic recording apparatus based on the principle of the dropping mercury electrode would provide a continuous record of the dissolved oxygen throughout the day. Briggs, Knowles and Scruggs, working at the Water Pollution Research Laboratory, have recently given a preliminary account of an apparatus for the continuous determination and recording of dissolved oxygen based on the well-known Winkler method, the optical density of the liberated iodine being measured by a photoelectric cell and recorded on a chart. Continuous records obtained in this way should prove useful in assessing any fluctuations in dissolved oxygen content due to variations in the organic pollution load, the effects of photosynthesis, and weather conditions such as sunshine, wind action and rainfall.

When the percentage saturation of dissolved oxygen falls below 57 per cent in a fishing stream, fish, especially game fish, are liable to be adversely affected. A desirable figure for fish is at least 75 per cent of saturation but many coarse fish can live in water with a dissolved oxygen content as low as 30 per cent of saturation. The concentration of dissolved oxygen seems to be of particular importance to fish when poisonous substances are present in the stream. Experiments carried out by the Water Pollution Research Laboratory indicate that the effect of toxic substances on fish is enhanced when the concentration of dissolved oxygen is low, and consequently it could happen that sub-lethal amounts of toxic substances might prove relatively innocuous during the day, when sufficient dissolved oxygen is present, but lethal at night when the dissolved oxygen concentration falls.

Lasleben has shown that very high concentrations of dissolved oxygen in water may prove dangerous to fish. He found that carp remained healthy in ponds containing dissolved oxygen between 125 per cent and 150 per cent of saturation but when the dissolved oxygen was greater than 150 per cent of saturation the fish developed maxillary diseases (e.g. diseases of the fins) and dropsy.

**AMMONIACAL NITROGEN**

Ammonia arises as a rule from the aerobic or anaerobic decomposition of nitrogenous organic matter and if present in a stream in appreciable amounts (say >0.2 p.p.m.) provides strong presumptive evidence of the presence of sewage or sewage effluent, especially if there is also a rise in the chloride content. In fact, the Royal
Commission on Sewage Disposal stated in their 8th Report that 'the most delicate chemical index of recent sewage pollution in a river water is the increase in the figure for ammoniacal nitrogen yielded by the water shortly below the outfall as compared with the water above'. The Commission, however, added that the ammoniacal nitrogen figure does not provide so good an index of the actually observed condition of the stream or of the polluting power of an effluent as does the B.O.D. test. It must also be remembered that a large number of trade wastes containing either ammonia or nitrogenous organic matter, for instance gas liquor, tannery effluents, dairy wastes, piggery wastes, and many chemical wastes, can cause an increase in the ammoniacal nitrogen content of a river.

Rivers known to be unpolluted generally contain extremely small amounts of ammoniacal nitrogen. Thus, in a survey of the unpolluted River Wharfe, the old West Riding of Yorkshire Rivers Board found that the ammoniacal nitrogen content of the river varied only between 0 and 0.17 p.p.m.

There is much evidence in the literature to show that ammonia and ammonium compounds even in relatively small amounts are toxic to fish and that the toxicity is affected by the pH value of the water. It is therefore desirable that a sewage effluent discharging to a small fishing stream should be well nitrified. Spicer from observations in the Trent River Board area states that where the ammoniacal nitrogen figure of a river water exceeds 3 p.p.m. few, if any, coarse fish are likely to be found and that even when the figure is over 1 p.p.m. the river is not very attractive to fish. Recent work suggests that it is the proportion of ammonia in the form of unionized ammonia (which increases with rise in pH value) rather than the total ammonia or the ammonium ion that is responsible for the toxic effects on fish (cf. also Chapter 7, page 168). For instance, Alabaster and Herbert showed that although Watford tap water (dissolved oxygen content 4.41 p.p.m.), to which was added 30 p.p.m. of ammoniacal nitrogen, was rapidly toxic to trout, yet if carbon dioxide (30 p.p.m.) was also present it lowered the pH value, and therefore the concentration of unionized ammonia, to such an extent that trout were not affected by the water after a 12-hour exposure period. More recently, Downing and Marks, following up earlier work by Wuhramann, have shown that the toxicity of solutions of unionized ammonia to rainbow trout is affected by the dissolved oxygen concentration of the water; the periods of survival of the fish in the range 0-0-0-1-96 p.p.m. of ammoniacal N increasing as the dissolved oxygen content rose from 1.5 to 8.5 p.p.m.

The presence of more than traces of ammoniacal nitrogen in river
winters used as sources of drinking-water is not as a rule regarded with favour by water undertakings using chlorine for germicidal purposes. Waters high in ammonia have a high chlorine demand and require much longer contact periods for satisfactory sterilization. This difficulty can be circumvented by using nitrifying filters to oxidize ammoniacal nitrogen to nitrate; according to Carey this was done during World War II by Coventry in connection with the treatment of River Avon water.

ORGANIC NITROGEN AND ALBUMINOID NITROGEN

Organic nitrogen is the organically bound nitrogen in nitrogenous organic matter and includes the nitrogen in proteins and their decomposition products such as amino-acids, organic bases and urea. Albuminoid nitrogen is that fraction of the organic nitrogen which is easily decomposed when the sample, previously freed from ammonia, is distilled with alkaline potassium permanganate according to a standard procedure (cf. Chapter 9, page 283). In raw sewages, the albuminoid nitrogen is usually about half of the total organic nitrogen but this relation does not necessarily hold in the cases of effluents and river waters. Although the estimation of albuminoid nitrogen still finds favour in most laboratories in this country, the determination of organic nitrogen is claiming many adherents who regard it as more accurate and reliable. Nevertheless, the albuminoid nitrogen estimation is easier and quicker to carry out—an important consideration in busy laboratories doing large numbers of routine samples—and in the author's opinion it gives all the information needed, namely a rough measure of the amount of nitrogenous organic matter present, animal or vegetable. Moreover, albuminoid nitrogen gives a measure of the relatively easily decomposable organic matter which from the standpoint of pollution is of greater significance than the total organic nitrogen. Organic nitrogen and albuminoid nitrogen are less valuable indices of pollution than the B.O.D. test. Albuminoid nitrogen values much above 0.2 p.p.m. in a stream should generally be regarded with some suspicion but it must be emphasized that algae and decaying vegetation can give fairly high albuminoid nitrogen values at certain times of the year.

THE RATIO OF AMMONIACAL NITROGEN TO ALBUMINOID NITROGEN

In the majority of sewages and sewage effluents the amount of ammoniacal nitrogen greatly exceeds the amount of albuminoid nitrogen. Consequently, a high ammoniacal nitrogen: albuminoid
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Nitrogen ratio in a river water is usually a good indication of the presence of sewage or sewage effluent. On the other hand in the case of vegetable pollution (e.g. peaty waters), the ammoniacal nitrogen is generally low and the albuminoid nitrogen relatively high and hence a low ammoniacal nitrogen:albuminoid nitrogen ratio is obtained. A much more reliable indication of vegetable pollution, however, is obtained by using a method proposed by Gibson\textsuperscript{17}, described below.

DIFFERENTIATION BETWEEN ANIMAL POLLUTION AND VEGETABLE POLLUTION

The differentiation between organic matter of animal origin and organic matter of vegetable origin is sometimes of great importance in helping to identify a discharge to a river and to locate the source of the pollution. Gibson\textsuperscript{17}, following up earlier work of Buydens, and Dixon and Jenkins, has shown that the ratio of oxygen absorbed from \(N\textsubscript{a}\textsuperscript{2}O\textsubscript{2}\) sodium hypochlorite in 4 hours at 80 ° F to oxygen absorbed from acid \(N\textsubscript{a}\textsuperscript{2}O\textsubscript{2}\) potassium permanganate in 4 hours at 80 ° F

is less than 1·0 for vegetable organic matter

and more than 1·0 for animal organic matter

This is illustrated by Table 62 which is based partly on the work of Gibson and partly on unpublished experiments carried out in the laboratories of the Mersey River Board.

Table 62. The \(Na\textsubscript{2}O\textsubscript{2}:KMnO\textsubscript{4}\) ratio for various wastes and polluted waters

<table>
<thead>
<tr>
<th>Wastes, etc., of vegetable origin ((Na\textsubscript{2}O\textsubscript{2}:KMnO\textsubscript{4} \text{ ratio } &lt; 1·0))</th>
<th>Wastes, etc., of animal origin ((Na\textsubscript{2}O\textsubscript{2}:KMnO\textsubscript{4} \text{ ratio } &gt; 1·0))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper making wastes</td>
<td>Sewage and Sewage effluents</td>
</tr>
<tr>
<td>Calico printing wastes</td>
<td>Farm drainage</td>
</tr>
<tr>
<td>Cotton bleaching wastes</td>
<td>Piggyery wastes</td>
</tr>
<tr>
<td>Brewery wastes</td>
<td>Dairy wastes</td>
</tr>
<tr>
<td>Vegetable casing wastes</td>
<td>Tannery wastes</td>
</tr>
<tr>
<td>Vegetable pickling wastes</td>
<td>Rivers polluted by any of the above wastes</td>
</tr>
<tr>
<td>Pea washing wastes</td>
<td>—</td>
</tr>
<tr>
<td>Coal washing effluents*</td>
<td>—</td>
</tr>
<tr>
<td>River waters polluted by any of the above wastes</td>
<td>—</td>
</tr>
<tr>
<td>Peaty river waters</td>
<td>—</td>
</tr>
</tbody>
</table>

* Coal-dust can be regarded as well-decomposed vegetable matter.

Quick results can often be obtained in Gibson’s procedure if the hypochlorite and permanganate estimations are carried out in 3
minutes instead of 4 hours, but the conclusions reached are then less reliable.

Certain sewage sludges (e.g. Imhoff tank sludge, digested sludge and activated sludge) appear to be exceptions to Gibson's generalization for they behave as if they were of 'vegetable' origin and give a ratio of less than 1.0.

**CHLORIDE**

Chloride is present as sodium chloride in urine to the extent of about 1 per cent. Hence sewage always contains chloride, the amount present depending upon the strength of the sewage, the presence of trade wastes containing chlorides, and the chloride content of the water supply. Chloride remains unaltered during the purification of sewage and consequently approximately the same value should be obtained at each stage of the purification process, otherwise the samples are not truly comparable.

The chloride content of various waters is shown in Table 63.

**Table 63. Average chloride content of various waters**

<table>
<thead>
<tr>
<th>Source</th>
<th>p.p.m. of chlorine, Cl⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rain water</td>
<td>2</td>
</tr>
<tr>
<td>Upland surface water</td>
<td>12</td>
</tr>
<tr>
<td>Unpolluted river water</td>
<td>up to 15</td>
</tr>
<tr>
<td>Spring water</td>
<td>25</td>
</tr>
<tr>
<td>Deep well water</td>
<td>50</td>
</tr>
<tr>
<td>Drinking water</td>
<td>10-20, but variable</td>
</tr>
<tr>
<td>Weak sewage</td>
<td>70</td>
</tr>
<tr>
<td>Medium sewage</td>
<td>100</td>
</tr>
<tr>
<td>Strong sewage</td>
<td>up to 500</td>
</tr>
<tr>
<td>Urine</td>
<td>4,500-5,000</td>
</tr>
<tr>
<td>Sea water</td>
<td>20,000</td>
</tr>
</tbody>
</table>

It will be observed from the table that sea water contains about 20,000 p.p.m. of Cl⁻. Hence, in tidal waters the Cl⁻ content may vary from a few p.p.m. up to about 20,000 p.p.m. depending upon the proportion of sea water present. The chloride figure at a particular point in an estuary may thus be used to calculate approximately the proportion of sea water at that point

$$\text{percentage of sea water present} = \frac{\text{Cl⁻ content in p.p.m.} \times 100}{20,000}$$

It must be pointed out, however, that the chloride figure can be fairly high in streams passing through salt-bearing strata or where there is pollution by trade discharges with a high salt content (e.g.
discharges of brine from a salt works or from water-softening plants using the base-exchange process. Sea water contains bromide to the extent of about 65 p.p.m. (expressed as Br) and a determination of the Cl:Br ratio, which is approximately 300:1 in sea water, can also be used as an index of contamination by tidal waters.

When the possibility of trade effluent pollution or contamination by sea water is ruled out, a sudden rise in the chloride content of a stream usually indicates the presence of sewage, sewage effluent, farm drainage or piggery waste. An excessive content of chloride in an inland stream may cause death of freshwater fish and of certain vegetation (cf. page 34).

NITRITES AND NITRATES

Nitrate represents the final oxidation product of ammonia, and therefore completely treated sewage contains a high proportion of nitrate. Thus, nitrate in a river water is generally an indication of the presence of treated sewage effluents. When percolating filters at a sewage disposal works are operating efficiently and are not overloaded, the final effluent should contain nitrate but little or no nitrite. Nitrification is much more intense at the higher temperatures of the summer months, when bacterial activity is greater, than during the colder winter months. In a badly worked or overloaded filter, where there is likely to be an oxygen deficiency or where faulty distribution of sewage takes place, nitrites tend to increase and nitrates to fall, probably due to reduction of NO$_2^-$ to NO$_3^-$ or to incomplete oxidation of ammonia; ‘ponding’ or choking of the filter is the probable result with production of unsatisfactory or bad effluents containing much nitrite (occasionally up to 20 p.p.m., as N). Thus, even a trace of nitrite in a river water may indicate pollution by imperfectly treated sewage, especially if the river water also shows increases in ammoniacal nitrogen and chloride (see page 395). Norwegian workers have suggested that the concentration of nitrite would be a useful criterion for assessing sewage pollution in Oslo harbour.

In most activated sludge plants it is generally considered uneconomic to carry the purification of sewage beyond the clarification stage; little or no nitrate may be produced and yet the effluent may be well clarified with a low B.O.D. and a low content of suspended solids. However, at two well-known activated sludge plants in this country (Mogden and Colne Valley), gas from the anaerobic digestion of the sewage sludges provides cheap power and this makes it an economic proposition to achieve a considerable degree of nitrification comparable to that obtained in percolating filters.
In highly polluted industrial rivers, such as the River Irwell in Lancashire, the presence of nitrates derived from sewage effluents is regarded by the river board as a great advantage because when the dissolved oxygen content of the river falls to zero, which happens frequently in warm weather during the summer months, nitrates supply combined oxygen and so tend to delay or prevent the onset of anaerobic conditions and the production of foul odours (cf. Chapter 3, page 55).

In fishing streams, the presence of nitrates may appear to be of lesser importance. But it must be remembered that a highly nitrified sewage effluent will contribute less ammoniacal nitrogen to a stream than a poorly nitrified effluent. Fish thrive better in a stream when the ammoniacal nitrogen content is low (cf. page 372). Moreover, many fishing streams during summer drought conditions may be depleted of dissolved oxygen to a dangerously low level and nitrates may stimulate the growth of algae and other green plants which by photosynthetic action (page 369) help to supply extra dissolved oxygen.

**Methylene Blue Stability Test**

Methylene blue is an intense blue organic dyestuff which in the presence of reducing agents is converted into a colourless compound known as leuco-methylene blue. This change of colour occurs at an oxidation-reduction potential which is not far removed from zero, as Table 64, compiled from a British Drug Houses publication\(^{24}\), shows.

<table>
<thead>
<tr>
<th>Percentage oxidation</th>
<th>Oxidation-reduction potential (V)</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>-0.040</td>
<td>Almost colourless</td>
</tr>
<tr>
<td>10</td>
<td>-0.018</td>
<td>Half colourd</td>
</tr>
<tr>
<td>50</td>
<td>+0.011</td>
<td></td>
</tr>
<tr>
<td>95</td>
<td>+0.049</td>
<td></td>
</tr>
<tr>
<td>98</td>
<td>+0.062</td>
<td>Almost fully blue</td>
</tr>
</tbody>
</table>

Thus, methylene blue serves as an indicator of approximately zero oxidation-reduction potential and it is this property that makes it of value in determining the stability of a sample. A stable effluent or river water is one which is not liable to undergo significant change, and which remains aerobic for a reasonable period of time (usually five days); in the stability test what we really determine is the time taken for the sample when incubated out of contact with air to use
ASPECTS OF RIVER POLLUTION

up, by bacterial action, all its available oxygen (dissolved oxygen as well as combined oxygen in the form of nitrite and nitrate). The work of HEUKELEKIAN and others has shown that when organic matter undergoes oxidation by bacterial action, the order in which the various sources of oxygen are utilized by bacteria is as follows: (i) dissolved oxygen; (ii) nitrates and nitrites; and (iii) sulphates. No nitrate reduction occurs until all the dissolved oxygen has disappeared, and methylene blue is not reduced until all the nitrates are used up. When all the oxygen in the form of dissolved oxygen and nitrate is exhausted, aerobic conditions give place to anaerobic conditions, sulphate is reduced to hydrogen sulphide, other evil-smelling products of anaerobic action are formed (cf. page 30), and methylene blue is reduced to the colourless leuco-compound.

Table 65. Analysis of activated sludge plant effluent passing the Royal Commission standards for B.O.D. and suspended solids, but failing the stability test

<table>
<thead>
<tr>
<th>pH value</th>
<th>Oxygen absorbed from permanganate in 3 mins. (27°C)</th>
<th>Oxygen absorbed from permanganate in 4 hours (27°C)</th>
<th>Oxidized nitrogen (nitrite + nitrate)</th>
<th>B.O.D. (5 days, 20°C)</th>
<th>Suspended solids</th>
<th>Methylene blue stability test</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7·8 p.p.m.</td>
<td>7·4 p.p.m.</td>
<td>22·0 p.p.m.</td>
<td>nil</td>
<td>11·6 p.p.m.</td>
<td>Failed in 18 hours (giving H₂S)</td>
</tr>
</tbody>
</table>

In the case of river waters, the methylene blue stability test gives some idea of the length of time aerobic conditions would be maintained assuming that no re-aeration takes place. A water failing the test in a short time (say, 18 hours or less) is usually grossly polluted by organic matter and liable to become septic and give rise to complaints from river users and others of smells. It is, therefore, particularly important that sewage effluents discharging to streams which are already polluted, or to streams which afford little dilution, should pass a stability test, otherwise there is a possibility of odour nuisance from the river.

The stability test is especially valuable in showing pollution in samples which have undergone anaerobic fermentation since in these cases the B.O.D. test is apt to give unreliable results (cf. page 387). This point can be illustrated by the analysis of an activated sludge plant effluent shown in Table 65.

It is to be noted that this effluent would have been passed as satisfactory if judged solely on the basis of the Royal Commission tests for B.O.D. and suspended solids. Its failure to pass the stability test showed that it was by no means satisfactory. In fact, it contained a considerable proportion of the polluting supernatant liquor.
INTERPRETATION OF CHEMICAL TESTS

from a sludge digestion plant which, as explained on page 391, has an abnormally low B.O.D. Subsequent investigation showed that a workman in charge had in error permitted this liquor to go to the activated sludge final settlement tanks instead of to the raw sewage inlet for treatment.

OXYGEN ABSORBED FROM ACID PERMANGANATE

("permanganate value")

In this country, this test is usually carried out in 3 minutes and in 4 hours.

The 3 minutes test measures the immediate oxygen demand of the sample due to oxidizable inorganic matter as well as to very easily oxidizable organic matter. Thus, a high 3 minutes permanganate figure is obtained in the presence of considerable amounts of ferrous salts, nitrites, sulphides, sulphites, thiosulphates, thiocyanates, phenols and formaldehyde. Trade wastes containing these substances (e.g. iron pickle liquor, mine waters, and gas liquor) will therefore give high 3 minutes permanganate values.

The 4 hours permanganate test is a simple and quick method of measuring approximately the oxidizable matter (organic and inorganic) in sewages, sewage effluents, trade effluents and river waters; a high value indicating as a rule organic pollution. In the case of a sewage effluent discharging to an inland stream providing a dilution of at least 8 vol., the 4 hours permanganate value of the effluent should not be greater than 15-20 p.p.m. Treated effluents from sewage works dealing with sewage containing gas liquor and certain other trade wastes sometimes exceed this limit though they may still satisfy the Royal Commission B.O.D. standard of 20 p.p.m. With stream waters, the 4 hours permanganate figure should not as a rule be greater than about 3-5 p.p.m. though a higher figure is permissible if peaty matter is present. Observations on rivers within the Trent River Board area suggest that there is a rough correlation between the 4 hours permanganate value and the prominent animal populations present in the water. Choice fish (trout and grayling) and caddis and may-flies were found in clean streams having an approximate 4 hours permanganate value ranging from 0-3 p.p.m.; chub, dace, water shrimps and snails were present when the permanganate value was about 3-6 p.p.m., whilst only coarse fish (roach and gudgeon) as well as hog-lice (Aellops) and leeches inhabited streams having a permanganate value of about 6-10 p.p.m.

No fish were observed when the permanganate value of a stream exceeded 10 p.p.m.

* Provided that inorganic pollution is absent, as indicated by a relatively low 3 minutes figure.
The 4 hours:3 minutes permanganate oxygen absorption ratio in a river water is of considerable significance and in many cases may provide an important clue to the cause of the pollution. Effluents from domestic sewage and river waters containing untreated or treated domestic sewage generally yield a ratio of about 3·0 but this ratio can be disturbed by the presence of certain trade wastes. For instance, gas liquor in a sewage or river water tends to lower this ratio considerably, often to a value around 2·0. These facts are illustrated by the data given in Tables 66-70 for various effluents and river waters in Lancashire.

Vegetable waste waters and streams polluted by such wastes usually have a high 4 hours:3 minutes ratio. This is illustrated by the figures shown in Table 70, from which it will be seen that the ratio lies between 4 and 10.

**Table 66.** Ratio 4 h:3 min permanganate oxygen absorption for a final effluent from domestic sewage (Bolton, Longworth)

<table>
<thead>
<tr>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 min</td>
<td>4 h</td>
</tr>
<tr>
<td>2.2.49</td>
<td>2.8</td>
<td>8.6</td>
</tr>
<tr>
<td>11.1.50</td>
<td>3.6</td>
<td>10.2</td>
</tr>
<tr>
<td>3.12.50</td>
<td>1.4</td>
<td>4.2</td>
</tr>
<tr>
<td>30.5.51</td>
<td>2.6</td>
<td>7.4</td>
</tr>
<tr>
<td>10.10.51</td>
<td>4.0</td>
<td>10.8</td>
</tr>
<tr>
<td>5.2.52</td>
<td>1.6</td>
<td>5.6</td>
</tr>
<tr>
<td>24.6.52</td>
<td>2.0</td>
<td>6.8</td>
</tr>
<tr>
<td>5.2.53</td>
<td>2.4</td>
<td>7.2</td>
</tr>
<tr>
<td>13.5.53</td>
<td>3.2</td>
<td>9.6</td>
</tr>
<tr>
<td>3.9.53</td>
<td>2.4</td>
<td>7.2</td>
</tr>
</tbody>
</table>

Average = 3.0

**Table 67.** Ratio 4 h:3 min permanganate oxygen absorption for a final effluent from sewage containing about 2 per cent by volume of gas liquor

<table>
<thead>
<tr>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3 min</td>
<td>4 h</td>
</tr>
<tr>
<td>6.8.47</td>
<td>20.8</td>
<td>42.2</td>
</tr>
<tr>
<td>16.12.47</td>
<td>23.4</td>
<td>54.0</td>
</tr>
<tr>
<td>11.2.48</td>
<td>20.4</td>
<td>44.4</td>
</tr>
<tr>
<td>24.6.48</td>
<td>12.4</td>
<td>37.6</td>
</tr>
<tr>
<td>28.4.49</td>
<td>25.2</td>
<td>51.4</td>
</tr>
<tr>
<td>13.10.49</td>
<td>15.6</td>
<td>31.8</td>
</tr>
<tr>
<td>18.5.50</td>
<td>30.8</td>
<td>62.8</td>
</tr>
<tr>
<td>19.10.50</td>
<td>14.0</td>
<td>30.8</td>
</tr>
<tr>
<td>18.4.51</td>
<td>19.0</td>
<td>42.6</td>
</tr>
<tr>
<td>31.5.52</td>
<td>13.2</td>
<td>29.6</td>
</tr>
</tbody>
</table>

Average = 2.1
### Table 68. Ratio of 4 h:3 min permanganate oxygen absorption for a river water polluted by gas liquor (Sankey Brook, at Penkford Bridge, Newton)

<table>
<thead>
<tr>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4.52</td>
<td>46-0</td>
<td>69-6</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.5.52</td>
<td>64-4</td>
<td>140-0</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.7.52</td>
<td>58-0</td>
<td>116-0</td>
<td>2.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11.12.52</td>
<td>51-2</td>
<td>92-0</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15.4.53</td>
<td>47-0</td>
<td>92-0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16.7.53</td>
<td>71-0</td>
<td>132-0</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.10.53</td>
<td>34-4</td>
<td>77-0</td>
<td>2.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.4.54</td>
<td>56-8</td>
<td>102-0</td>
<td>1.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14.7.54</td>
<td>26-8</td>
<td>53-0</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12.10.54</td>
<td>36-0</td>
<td>68-0</td>
<td>1.9</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Average = 2.0

### Table 69. Ratio of 4 h:3 min permanganate oxygen absorption for rivers above and below gasworks discharges of gas liquor

<table>
<thead>
<tr>
<th>River</th>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Douglas</td>
<td>above gasworks discharge</td>
<td>3.753</td>
<td>6.0</td>
<td>18-0</td>
<td>3.0</td>
<td>1.6</td>
</tr>
<tr>
<td>R. Douglas</td>
<td>below gasworks discharge</td>
<td>3.753</td>
<td>59-8</td>
<td>95-0</td>
<td>1.6</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>R. Irwell</td>
<td>above gasworks discharge</td>
<td>6.533</td>
<td>3.6</td>
<td>12-0</td>
<td>3.3</td>
<td>2-1</td>
</tr>
<tr>
<td>R. Irwell</td>
<td>below gasworks discharge</td>
<td>6.533</td>
<td>19-0</td>
<td>40-0</td>
<td>2.1</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>R. Medlock</td>
<td>above gasworks discharge</td>
<td>15.433</td>
<td>1-6</td>
<td>3.3</td>
<td>3-3</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>R. Medlock</td>
<td>below gasworks discharge</td>
<td>15.433</td>
<td>320-0</td>
<td>530-0</td>
<td>1-7</td>
<td>4 h:3 min</td>
</tr>
</tbody>
</table>

### Table 70. Ratio of 4 h:3 min permanganate oxygen absorption for vegetable wastes and streams polluted by vegetable wastes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
<th>Date</th>
<th>Permanganate oxygen absorption p.p.m.</th>
<th>Ratio 4 h:3 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pea washing wastes</td>
<td>688</td>
<td>3,000</td>
<td>4-4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stream below discharge of pea washing wastes</td>
<td>66-0</td>
<td>282-0</td>
<td>4-3</td>
<td>4-4</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>Potato washing wastes</td>
<td>400</td>
<td>2,300</td>
<td>5-8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carrot canning wastes</td>
<td>151</td>
<td>1,450</td>
<td>9-7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vegetable pickle factory discharge</td>
<td>17-6</td>
<td>73-0</td>
<td>4-3</td>
<td>4-4</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>Dehydrated vegetable wastes</td>
<td>146</td>
<td>742</td>
<td>5-1</td>
<td>4-4</td>
<td>4 h:3 min</td>
</tr>
<tr>
<td>Brewery wastes</td>
<td>320</td>
<td>2,080</td>
<td>6-5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
382 ASPECTS OF RIVER POLLUTION

BIOCHEMICAL OXYGEN DEMAND (B.O.D.)

This determination was first recommended as a standard test of purity for sewage effluents and river waters by the Royal Commission on Sewage Disposal under the rather cumbersome title 'dissolved oxygen taken up in 5 days at 65° F.' Later, Lederer with the American genius for inventing concise and pithy expressions happily re-named it 'Biochemical Oxygen Demand' which was subsequently abbreviated to 'B.O.D.' by which it eventually came to be known. It is questionable whether the test would ever have become so popular without the backing of so distinguished a body as the Royal Commission. It could scarcely have been realized at the time that the test was destined to become the subject of considerable controversy and of a much more voluminous literature than any other comparable determination.

The B.O.D. determination, being a biochemical test dependent upon the activities of bacteria, is subject to a number of errors. Indeed, Weston28 has drawn attention to the fact that at least eighteen variables may have an important influence on the test. Even a short, and by no means exhaustive, list would have to include the following factors:

Variation in temperature

The temperature recommended by the Royal Commission on Sewage Disposal for the determination of B.O.D. was 65° F (= 18.3° C). The Ministry of Housing and Local Government29 has now suggested that in order to bring British practice into line with American and Continental procedure, the standard temperature for the test should be 20° C. It is very important that this temperature should be correct and that it should be kept reasonably constant over the period of 5 days. It can be calculated from equation (2) on page 148 (Chapter 6) that an increase or a decrease of only 1° C means an increase or decrease respectively in B.O.D. of 4.7 per cent.

Composition of dilution water

As a result of the recommendations of the Royal Commission on Sewage Disposal, it has hitherto been the practice in Great Britain to use aerated tap water as dilution water for the determination of B.O.D. The variation in the composition of tap water in different localities has been suggested as a reason for many of the discrepancies in B.O.D. results obtained in different laboratories examining the same sample. Moreover, the tendency nowadays to sterilize domestic water supplies introduces an additional hazard in the shape of free chlorine which has a marked adverse effect on bacterial activity. Hence the Ministry of Housing and Local Government29 has,
following American practice, now recommended the use of a standard synthetic dilution water instead of tap water. Recent experiments by Wheatland and Smith, of the Water Pollution Research Laboratory, have indicated that this standard dilution water used for the determination of the B.O.D. of sewage should be freshly prepared, or, if this is not practicable, stored for not more than one week in thoroughly cleaned containers. If water stored for longer periods is used, much higher B.O.D. results are obtained since the ammonium compounds originally present in the synthetic water undergo nitrification and the active growths of nitrifying bacteria then tend to cause nitrification of ammonia in the sewage sample.

According to Sawyer and his co-workers, the basic requirements of a suitable B.O.D. dilution water are: correct pH limits, proper salinity, reasonable buffer capacity, the presence of necessary nutrients, the absence of toxic substances (e.g. chlorine, metallic contaminants, etc.) and finally the presence of a balanced and viable seeding material. It is not always easy to know whether all these requirements are satisfied and these authors have therefore proposed the use of two primary standards, i.e. solutions containing 300 p.p.m. of pure glucose (5-day B.O.D. at 20°C = 224 p.p.m.) and 300 p.p.m. of pure glutamic acid (5-day B.O.D. at 20°C = 217 p.p.m.) for use in checking and standardizing B.O.D. results and techniques.

The use of river water as dilution water in the B.O.D. test is not to be recommended since it has been shown by Lamb and Jenkins that the results obtained on different days showed considerable variation.

Dilution used

The B.O.D. of a sample may depend to a considerable extent on the particular dilution used. It is therefore advisable to put on several dilutions and to base the value on the dilution showing about 50 per cent depletion of the dissolved oxygen. In the case of certain trade wastes (e.g. gas liquor) the B.O.D. is so largely dependent on the dilution that the test becomes quite unreliable as a measure of the strength of the waste, and it is better to adopt the 4 hours permanganate test.

Presence of bacteriostatic and bactericidal substances

The presence in sewage or trade wastes, or in the dilution water, of substances inhibiting or preventing altogether the growth of bacteria can cause huge errors in a B.O.D. determination and may render the test useless in some cases unless certain precautions are adopted.
Acids and alkalis have a marked effect upon bacterial activity (cf. Chapter 6, page 120) and samples which are acid or alkaline should be neutralized to bring them within the pH range 6.5-8.3 and then seeded with sewage.

Toxic metals (e.g. copper, lead, mercury) are particularly undesirable in the sample or dilution water (cf. this Chapter, page 389) on account of their inhibiting effect even in small quantities on bacterial activity. Copper is especially notorious in this respect and the dilution water used should contain less than 0.01 p.p.m. of copper otherwise a marked depressing effect on the B.O.D. will be obtained.

River waters and trade wastes containing both organic pollution and metallic contaminants are likely to give misleadingly low B.O.D. results and the use of the 4 hours permanganate test is advised in order to assess the amount of organic matter present.

Nitrification

It has been reported by many workers 32-34 that sewage effluents which are in a state of incipient nitrification can show misleadingly high values in the standard 5-day B.O.D. test and yet be quite satisfactory. This is due to the fact that such effluents not only have an oxygen demand caused by oxidation of carbonaceous matter but also an oxygen demand due to nitrification (i.e. oxidation of ammoniacal nitrogen and nitrite nitrogen to nitrate nitrogen). The same phenomenon has been observed by Abbott 35 with some river waters. In one example given by Lockett 33 the 5-day B.O.D. of a sewage effluent was 31.4 p.p.m. of which only 9 p.p.m. was due to the actual carbonaceous pollution whilst the remaining 22.4 p.p.m. was accounted for by the conversion of ammoniacal nitrogen to oxidized nitrogen (i.e. nitrite + nitrate) by nitrifying organisms.

Methods of preventing the onset of nitrification during the 5-day B.O.D. test include the following:

(i) Flash pasteurization of the sample at 60-80° C, thus destroying the organisms responsible for nitrification 36.
(ii) Chlorination of the sample, excess of chlorine being afterwards removed with sodium sulphite 36.
(iii) Acidification to pH 2-3 to sterilize the sample, followed by neutralization 37.

In these three cases, the usual B.O.D. procedure is then followed using dilution water seeded with settled domestic sewage. It is important that the sewage used for seeding should be free from nitrifying organisms 38.

(iv) Abbott 35, 39, 40 has found that methylene blue suppresses
nitrification but does not influence the rate of oxidation of carbonaceous matter. Hence, errors due to the occurrence of nitrification were eliminated by adding a small proportion of methylene blue (6 ml. of a 0·05 per cent aqueous solution) to each litre of the dilution water used in the B.O.D. test and determining dissolved oxygen before and after incubation by the Rideal-Stewart method.

The effect of nitrification is of considerable significance when effluents from an activated sludge plant (containing much ammonia but little or no nitrate) and from a biological filtration plant (rich in nitrifying organisms) are mixed or discharged to a comparatively small stream in close proximity. In this connection Stones has made the interesting observation that mixtures of these two types of sewage effluent can have biochemical oxygen demands greater than what would be expected from the values obtained for the individual effluents. The results of an experiment of this kind, taken from his paper, are shown in Table 71.

Table 71. B.O.D. of mixtures of activated sludge effluents and filter effluents from plants treating the same sewage

<table>
<thead>
<tr>
<th>Activated sludge (Sheffield bi-purification) effluent % by volume</th>
<th>Filtration plant effluent % by volume</th>
<th>B.O.D. of mixture p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>12·6</td>
</tr>
<tr>
<td>10</td>
<td>90</td>
<td>16·0</td>
</tr>
<tr>
<td>20</td>
<td>80</td>
<td>18·8</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>20·2</td>
</tr>
<tr>
<td>40</td>
<td>60</td>
<td>19·6</td>
</tr>
<tr>
<td>50</td>
<td>50</td>
<td>18·4</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>17·0</td>
</tr>
<tr>
<td>70</td>
<td>30</td>
<td>14·4</td>
</tr>
<tr>
<td>80</td>
<td>20</td>
<td>12·0</td>
</tr>
<tr>
<td>90</td>
<td>10</td>
<td>7·8</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>6·0</td>
</tr>
</tbody>
</table>

It will be seen from this table that as the proportion of activated sludge effluent in the mixture increases the B.O.D. rises steeply from 12·6 p.p.m., when no activated sludge effluent is present, to a maximum of 20·2 p.p.m. (i.e. very slightly above the Royal Commission standard for sewage effluents), when 30 per cent by volume of activated sludge effluent is present thereafter falling rapidly until the B.O.D. of the 100 per cent activated sludge effluent is 6·0 p.p.m. These results are explained by Stones on the assumption that the increase in B.O.D. from 12·6 to 20·2 p.p.m. is due to the occurrence of nitrification, i.e. oxidation of ammonia in the activated sludge.
effluent by nitrifying bacteria present in the filter effluent at the expense of the dissolved oxygen. It is, therefore, quite conceivable that two satisfactory effluents having B.O.D. values well within the Royal Commission standard of 20 p.p.m. might on admixture give an unsatisfactory effluent with a B.O.D. considerably above the Royal Commission standard. Moreover, the discharge of such a mixed effluent to a small stream might lead to marked deoxygenation of the water to the detriment of any fish life present.

Presence of nutrient materials

Bacteria require for their growth and activities the presence of an adequate supply of mineral nutrients. Many years ago, Lea and Nichols concluded from experiments on B.O.D. determinations of sewage and industrial wastes, using plain and supplemented bicarbonate dilution waters, that unless sufficient mineral nutrients (especially nitrogen and phosphorus) were present to satisfy the nutritional requirements of the bacteria, low B.O.D. results were obtained with certain trade wastes. They found that various types of paper-mill waste did in fact give greatly increased B.O.D. values (often two to five times as great) when instead of using a plain bicarbonate dilution water use was made of a supplemented dilution water containing magnesium sulphate, calcium phosphate, potassium dihydrogen phosphate and ammonium sulphate. On the other hand, with sewage and with pea canning wastes, which contain adequate amounts of nitrogen and phosphorus, there was no appreciable difference between B.O.D. determinations using plain and supplemented dilution waters. The results of Lea and Nichols appeared to indicate that an adequate supply of nitrogen and phosphorus would be afforded if the B.O.D. dilutions contained about 0.2-0.5 p.p.m. of nitrogen and about 0.02 p.p.m. of phosphorus. Sawyer and his associates have shown that certain industrial wastes are deficient in nitrogen or phosphorus or both. For instance, cotton kier liquor contains insufficient nitrogen; brewery waste is deficient in both nitrogen and phosphorus; and chrome tannery waste, although rich in nitrogen, contains inadequate amounts of phosphorus. Low B.O.D. values are therefore likely to be obtained with these and other mineral-deficient wastes unless the deficiencies are supplied in the dilution waters. Most stream waters probably contain sufficient mineral salts to give satisfactory B.O.D. results but difficulties may arise when a stream consists largely of trade effluents.

Seeding with bacteria

When determining the B.O.D. of sewages, sewage effluents, a few trade wastes (e.g. dairy wastes and piggery wastes) and most river
waters, inoculation is rarely necessary since the essential bacterial flora will be present. In the case of certain trade wastes and with samples which are acid or alkaline and therefore require neutralization, seeding with bacteria may be essential and for this purpose it has been the practice to add fresh settled sewage or sewage effluent (1 ml.) to the dilution water (1 l.). It has, however, been shown by Sawyer and his co-workers that this type of seed is not uniform in character and viability and gives results which differ according to the source of the sewage when tests are carried out on certain pure organic compounds of known B.O.D. (cf. page 383). Zschunpfenning and Nichols explain these variations in the character of the inoculum on the basis of changes in the relative proportions of protozoa and bacteria in the sewage and showed that if an inoculum is prepared by filtration through a suitable sintered glass filter so as to remove protozoa, satisfactory and reproducible B.O.D. results are obtained. Tyler and Gunter found that the standard method of seeding was unsatisfactory in the case of sulphite waste liquor (a waste of very high B.O.D. obtained in the manufacture of pulp for paper making by digesting wood chips with calcium bisulphite solution) and they recommend the use of a filtered soil extract as inoculum.

Presence of anaerobic organisms
In samples where anaerobic organisms predominate (e.g. septic sewage, digested sludges, septic river muds, supernatant liquor from sludge digestion tanks), a lag period takes place during the first 2 or 3 days resulting in an abnormally low B.O.D. figure (see Figure 26, page 391).

Miscellaneous sources of error
There are many other possible sources of error in the B.O.D. test in addition to those already discussed. For instance, the presence of certain interfering chemical compounds (e.g. ferrous salts, ferric salts, nitrates, sulphites) can cause inaccuracies; methods for overcoming these interferences have been given in Chapter 9. Again, variations in the size of bottle used resulting in a different ratio of internal surface to volume may have some influence on bacterial activity. A discussion of various minor errors in the B.O.D. test is given by Lawes.

Comparison of B.O.D. and permanganate tests
Both these tests, whilst quite distinct and showing in general little correlation, occupy an important place in analysis in the assessment of organic pollution for they estimate the amount of oxygen utilized
in the oxidation of the organic matter in a sample and therefore give an approximate measure of the amount of organic material present. But whilst the B.O.D. is a biochemical test measuring the amount of organic matter oxidized as a result of the activities of aerobic bacteria under prescribed conditions (5 days, 20° C), the 4 hours permanganate test is a purely chemical test measuring the amount of organic matter oxidized chemically by an acid solution of N/80 potassium permanganate under another set of arbitrary conditions (4 hours, 27° C). It is not, therefore, to be expected that these two tests will give parallel results. The 4 hours permanganate test has the merits of simplicity and of giving a quick result. The B.O.D. test takes considerably longer and is more complicated but nevertheless reproduces more closely the conditions of oxidation taking place naturally in a river.

Generally speaking, the B.O.D. determination is the most useful and sensitive test for the detection and measurement of organic pollution, especially nitrogenous organic matter such as sewage, farm drainage, dairy wastes, gelatine wastes, food processing wastes and cannerly wastes. This is illustrated by the analytical data given in Table 72.

<table>
<thead>
<tr>
<th>pH value</th>
<th>( \text{min permanganate test p.p.m.} )</th>
<th>( \text{4 hours permanganate test p.p.m.} )</th>
<th>Suspended solids</th>
<th>Volatile solids</th>
<th>Total p.p.m.</th>
<th>Nitrite nitrogen p.p.m.</th>
<th>Nitrate nitrogen p.p.m.</th>
<th>Methylene blue stability test</th>
<th>B.O.D. (5 days, 20° C) p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3.2</td>
<td>3.0</td>
<td>6.8</td>
<td>3.4</td>
<td>4.4</td>
<td>5.0</td>
<td>4.5</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>River</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Urudlis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Farm</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>washed out by drainage</td>
<td>16</td>
<td>11</td>
<td>12</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>untreated sewage by dairy</td>
<td>15</td>
<td>11</td>
<td>12</td>
<td>6</td>
<td>4</td>
<td>2</td>
<td>8</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>1.5</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Volatile solids</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>trace</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Total p.p.m.</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Nitrite nitrogen p.p.m.</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Nitrate nitrogen p.p.m.</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
<td>nil</td>
</tr>
<tr>
<td>Methylene blue stability test</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>B.O.D. (5 days, 20° C) p.p.m.</td>
<td>39.0</td>
<td>36.0</td>
<td>36.0</td>
<td>36.0</td>
<td>40.9</td>
<td>32.3</td>
<td>76.0</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>Ammoniacal nitrogen p.p.m.</td>
<td>0.70</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
<td>0.92</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>Albuminoid nitrogen p.p.m.</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>0.24</td>
<td>Failed</td>
<td>Failed</td>
</tr>
<tr>
<td>Dissolved oxygen, % of saturation</td>
<td>37</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>9</td>
<td>Failed</td>
<td>Failed</td>
</tr>
</tbody>
</table>

* Stream bed showed signs of sewage pollution (e.g. sewage fungus).

It will be observed from Table 72 that in all cases the B.O.D. figure shows unmistakably the presence of organic pollution whereas the 4 hours permanganate test gives low values and shows itself to be
unreliable as a test for organic matter. Most striking of all these analyses is that of the river polluted by dairy wastes where the B.O.D. is about thirteen times the permanganate value and the latter scarcely shows the polluting character of the sample. It is also noteworthy that the Methylene blue stability test proves its value in all these cases in indicating pollution.

The Royal Commission on Sewage Disposal recommended the B.O.D. test for sewage effluents and for stream waters in preference to the 4 hours permanganate test because the B.O.D. was found to be a more sensitive test for organic pollution and, moreover, initiated as far as is possible in a laboratory test the actual process of deoxygenation that takes place in a stream. They also showed that while the permanganate test often gave approximately the same figure for a stream polluted either by tank effluent or by a filter effluent, the B.O.D. was much higher when the river was polluted by tank effluent. As a result of extensive investigations by the Royal Commission, the 5-day B.O.D. value was adopted as 'the most trustworthy chemical index of the actual state of a stream', and they found that if this figure did not exceed 4 p.p.m. the river was normally free from signs of pollution. This limiting figure of 4 p.p.m. was the foundation upon which they based the well-known classification of rivers according to their B.O.D. (see Chapter 14, pages 542–5). Also, as already pointed out, the B.O.D. of a sewage effluent discharging to a stream, where it receives at least an 8-fold dilution by clean water, should not, according to the Royal Commission standard, exceed 20 p.p.m.

Some limitations of the B.O.D. as an indication of organic pollution must now be pointed out. Certain metals (e.g. lead, copper, mercury, chromium present as chromate) are toxic to bacteria even in low concentrations. Since the B.O.D. is so dependent on the activities of bacteria it is naturally affected to a marked degree by toxic substances which may have little or no influence on the 4 hours permanganate value. For instance, a recent report of an American research committee shows that as regards effect in the determination of the B.O.D. of sewage by the dilution method the toxicity of mercury increases slowly from 0·02–0·2 p.p.m. of mercuric chloride, and above 0·2 p.p.m. the toxicity rises steeply until at a concentration of about 2 p.p.m. of mercuric chloride the 5-day B.O.D. of the sewage is depressed to zero. Again, Placak, Ruchhoft and Snapp have reported that as little as 0·01 p.p.m. of copper and more than 0·3 of chromium (present as chromate) have a marked depressing effect on the B.O.D. of sewage; in the case of copper they found that the B.O.D. was depressed by about 5 per cent by 0·01 p.p.m. of copper, 23 per cent by 0·45 p.p.m., and 66 per cent by 1·6 p.p.m. A B.O.D. of about 80 per cent of the true value was

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obtained in the presence of 0-9 p.p.m. of chromium (present in the hexavalent form as chromate). Some workers (e.g. COBURN) have suggested that chromium present in the trivalent state does not cause much trouble biologically, but the report of an American research committee suggests that as regards effect on B.O.D. trivalent chromium is somewhat more toxic than chromate in the range 1-10 p.p.m. of chromium. KALABINAS found that as little as 0-1 p.p.m. of lead retarded the biochemical oxidation of organic matter. DAWSON and JENKINS have shown that 1-100 p.p.m. of many metallic ions (e.g. zinc, copper, chromium, nickel and cadmium) caused a marked reduction in the rate of oxygen uptake by activated sludge.

As an illustration of the effect of a toxic metal on B.O.D., Table 73 shows the analysis of stream water polluted by copper and much fatty organic material.

| pH value | 7-1 |
| 3 min permanganate value | 14.2 p.p.m. |
| 4 h permanganate value | 64.6 p.p.m. |
| Nitrite nitrogen | nil |
| Nitrate nitrogen | 4.0 p.p.m. |
| Ammoniacal nitrogen | 0.7 p.p.m. |
| Albuminoid nitrogen | 0.26 p.p.m. |
| B.O.D. (5 days, 20°C) | 0.26 p.p.m. |
| Copper (settled sample) | 5.8 p.p.m. |
| Copper (shaken sample) | 30 p.p.m. |
| Suspended solids \ volatile | 81 p.p.m. |
| Total solids | 437 p.p.m. |

It will be observed that, owing to the presence of copper, the B.O.D. is abnormally low in comparison with the 4 hours permanganate value.

Thus, the available evidence suggests that when small amounts of toxic metallic ions are present in organically polluted samples, an abnormally low B.O.D. figure can be expected owing to the suppression of bacterial activity. Other bactericides present in trade wastes (e.g. phenols, formaldehyde, free chlorine, cyanides, etc.) have a similar suppressing effect on B.O.D. In such cases, the B.O.D. test cannot be safely used as a measure of any organic pollution present and it is better to rely upon the permanganate test which, in general, is uninfluenced by the presence of bactericidal compounds. Among important trade wastes giving comparatively low B.O.D. values for this reason are gas liquor, wastes containing formaldehyde, TNT wastes, and plating wastes.
Supernatant liquor from plants digesting sewage sludge invariably gives a 5-day B.O.D. figure which is very much below the value which might be expected from a consideration of the other analytical data. This is illustrated by Table 74 which gives analytical results for a sample of supernatant liquor from a plant digesting a mixture of primary and activated sludges.

| pH value | 7.8 |
| 4 h permanganate value | 490 p.p.m. |
| 5-day B.O.D. (18.3°C) | 193 p.p.m. |
| Ammoniacal nitrogen | 440 p.p.m. |
| Albuminoid nitrogen | 78 p.p.m. |
| Mineral suspended solids | 320 p.p.m. |
| Volatile suspended solids | 750 p.p.m. |
| Total solids | 2,070 p.p.m. |
| Total solids | 2,930 p.p.m. |

Investigation of the B.O.D. of this sample for various periods of time up to 9 days showed that a lag period occurred during the first few days resulting in an abnormally low 5-day B.O.D. After about 5 days, however, the oxygen demand increased rapidly as shown graphically in Figure 26. Since supernatant liquor is rich in anaerobic organisms, it is probable that the cause of the lag period is related to a change from an anaerobic type of fermentation to an aerobic type. Any liquor which has undergone anaerobic fermentation (e.g., septic sewage) can be expected to behave in a similar way and show a tendency to yield low B.O.D. values.

In conclusion, it can be said that the B.O.D. estimation still remains the best available single test for assessing organic pollution.
but its errors, shortcomings and limitations must be borne in mind and the result of any test correlated with the other analytical data.

**THE RATIO OF THE B.O.D. TO THE 4 HOURS PERMANGANATE VALUE**

The 5-day B.O.D. of crude domestic sewage is usually about 2-4 times the 4 hours permanganate value and B.O.D.:permanganate ratios of a similar order of magnitude or even higher are generally obtained with trade wastes rich in carbohydrates and with such nitrogenous organic wastes as dairy wastes, piggery wastes and vegetable and other food processing wastes. The B.O.D.:permanganate ratio is, however, upset by the presence of certain non-nitrogenous organic trade wastes and by trade wastes containing toxic substances (e.g. gas liquor, chemical trade wastes, and wastes containing metallic contaminants). This is illustrated by Table 75, taken from a paper by Hewitt57, comparing the B.O.D. and 4 hours permanganate figures for sewages at four Birmingham sewage works.

**Table 75. Comparison of B.O.D. and 4 hours permanganate figures for different types of sewage (Birmingham)**

<table>
<thead>
<tr>
<th>Name of works</th>
<th>Character of sewage</th>
<th>5-day B.O.D. value p.p.m.</th>
<th>4 h permanganate value p.p.m.</th>
<th>Ratio B.O.D.: permanganate value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barston</td>
<td>Domestic</td>
<td>236</td>
<td>59</td>
<td>4</td>
</tr>
<tr>
<td>Colehill</td>
<td>Domestic</td>
<td>229</td>
<td>76-5</td>
<td>3</td>
</tr>
<tr>
<td>Yardley</td>
<td>Industrial*</td>
<td>222</td>
<td>120</td>
<td>1-8</td>
</tr>
<tr>
<td>Saltley</td>
<td>Industrial*</td>
<td>264</td>
<td>159</td>
<td>1-66</td>
</tr>
</tbody>
</table>

*Contains large proportion of metallic trade wastes.

It will be seen from this table that there is a tendency for the trade wastes to lower the B.O.D.:permanganate ratio. To explain these results, Hewitt suggests that whilst the permanganate test indicates the actual amount of organic impurity to be treated, the B.O.D. is more of an indication of the relative ease with which biochemical oxidation takes place. The effect of inhibitory trade wastes in lowering the B.O.D.:permanganate ratio is also strikingly shown by results obtained at Huddersfield by Goldthorpe and Nixon58. They found that by mixing chemical trade wastes (containing iron, organic chemicals and dyestuffs) with sewage in varying proportions the B.O.D.:permanganate ratio varied from as little as 0-2, when only chemical wastes were present, to over 3-0 when only sewage was present, with intermediate values dependent on the relative proportions of chemical wastes and sewage.
Although, as a rule, when inhibitory trade wastes are absent, sewages and tank effluents as well as imperfectly purified sewage effluents give high B.O.D.:permanganate ratios (over 1·0), well-purified sewage effluents and good effluents from the treatment of nitrogenous organic trade wastes give ratios less than 1·0 (i.e. the B.O.D. is less than the permanganate value). River waters relatively free from organic pollution (e.g. the upper reaches of many rivers known to be unpolluted) also give, in general, B.O.D.:permanganate ratios less than 1·0. When a ratio considerably greater than 1·0 is found in a river water, it is usually an indication of pollution by such discharges as sewage, farm drainage, dairy wastes, vegetable or other food processing wastes, or cotton finishing wastes containing starch, and in these cases a bad immediate effect on the river can be expected as regards deoxygenation. Obviously a river water, even if polluted, can give a ratio less than 1·0 if inhibitory trade wastes containing substances toxic to bacteria are present (acid and alkaline wastes, chemical wastes, gas liquor and metallic contaminants), and in these cases there would be a considerable adverse effect upon the self-purification of the stream.

**Effect of sewage discharges to rivers on analytical results**

The discharge of sewage or poorly treated sewage to a river has a pronounced effect on most of the chemical tests applied to stream waters, as shown in Table 76 by typical examples of Lancashire and Cheshire rivers. It will be seen that the effect of sewage or unsatisfactory sewage effluents on the analytical data is to cause decreases in dissolved oxygen and increases in the 3 minutes and 4 hours permanganate figures, chloride, suspended solids, B.O.D., and ammonia and albuminoid nitrogen. As already pointed out (page 372), the increase in the ammonia nitrogen figure affords a specially delicate chemical test for detecting sewage pollution. There is often an increase in nitrite nitrogen but nitrite being rather unstable and liable to undergo either oxidation in the stream or denitrification or reduction to nitrogen, is not always detectable. Where there is little or no nitrate present, the river below a sewage outfall is liable to fail the Methylene blue stability test and to cause odour nuisance, especially if the dilution available is low.

**Hardness**

The undesirability of hardness in river water used for steam raising and for most industrial purposes has already been emphasized previously (see Chapter 5, page 100).
Hardness is due mainly to the presence of bicarbonates of calcium and magnesium ('temporary' or 'carbonate' hardness) or to sulphates and chlorides of calcium and magnesium ('permanent' or 'non-carbonate' hardness). As a rule, any hardness due to calcium predominates greatly over that due to magnesium.

<table>
<thead>
<tr>
<th>River</th>
<th>Nature of discharge</th>
<th>Chlorides</th>
<th>Permanganate</th>
<th>Sulphates</th>
<th>Ammonia</th>
<th>Nitrate</th>
<th>Nitrogen</th>
<th>B.O.D.</th>
<th>Total solids</th>
<th>Methylene blue reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>R. Roe above</td>
<td></td>
<td>—</td>
<td>0.2</td>
<td>1.1</td>
<td>nil</td>
<td>0.42</td>
<td>nil</td>
<td>1.6</td>
<td>0.6</td>
<td>Passed</td>
</tr>
<tr>
<td>R. Roe below</td>
<td></td>
<td>86</td>
<td>80</td>
<td>1.1</td>
<td>1.5</td>
<td>25.3</td>
<td>nil</td>
<td>1.6</td>
<td>800</td>
<td>Passed</td>
</tr>
<tr>
<td>Stock Beck</td>
<td></td>
<td>15</td>
<td>0.4</td>
<td>2.0</td>
<td>1.2</td>
<td>0.0</td>
<td>nil</td>
<td>2.0</td>
<td>0.0</td>
<td>Passed</td>
</tr>
<tr>
<td>Stock Beck</td>
<td></td>
<td>45</td>
<td>0.4</td>
<td>17.4</td>
<td>14.0</td>
<td>0.0</td>
<td>1.5</td>
<td>20.1</td>
<td>18</td>
<td>Failed</td>
</tr>
<tr>
<td>B. Als above</td>
<td></td>
<td>22</td>
<td>0.0</td>
<td>0.0</td>
<td>0.0</td>
<td>0.02</td>
<td>nil</td>
<td>1.5</td>
<td>7.0</td>
<td>Failed</td>
</tr>
<tr>
<td>B. Als below</td>
<td></td>
<td>74</td>
<td>0.2</td>
<td>19.2</td>
<td>13.3</td>
<td>2.5</td>
<td>2.4</td>
<td>26.0</td>
<td>10.8</td>
<td>Passed</td>
</tr>
<tr>
<td>R. Calder</td>
<td></td>
<td>23</td>
<td>1.3</td>
<td>2.0</td>
<td>0.0</td>
<td>0.00</td>
<td>nil</td>
<td>2.4</td>
<td>1.1</td>
<td>Failed</td>
</tr>
<tr>
<td>R. Calder</td>
<td></td>
<td>31</td>
<td>4.6</td>
<td>19.2</td>
<td>25.1</td>
<td>1.0</td>
<td>0.5</td>
<td>13.1</td>
<td>6</td>
<td>Passed</td>
</tr>
</tbody>
</table>

A convenient classification of waters according to their hardness is given in a report published for the Ministry of Health given in Table 77.

<table>
<thead>
<tr>
<th>Hardness (expressed as p.p.m. of CaCO₃)</th>
<th>Description of water</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-50</td>
<td>Soft</td>
</tr>
<tr>
<td>50-100</td>
<td>Moderately soft</td>
</tr>
<tr>
<td>100-150</td>
<td>Slightly hard</td>
</tr>
<tr>
<td>150-200</td>
<td>Moderately hard</td>
</tr>
<tr>
<td>200-300</td>
<td>Hard</td>
</tr>
<tr>
<td>Over 300</td>
<td>Very hard</td>
</tr>
</tbody>
</table>
A connection between high carbonate hardness and organic pollution has been reported by Heisen and others to exist in the case of ground waters, and is ascribed to the increased solubility of calcium carbonate in the presence of proteins, humus and weak acids produced by the oxidation of organic matter.

The hardness of a river water is of considerable significance in connection with the discharge of effluents containing toxic metallic ions. In the discussion on the effect of metallic pollutants on fish (Chapter 7, pages 159-62) it was pointed out that zinc and lead in particular are much less toxic to fish in hard waters containing considerable amounts of calcium salts than in soft waters.

**ALKALINITY, ACIDITY AND pH**

It has been explained in a previous chapter (see Chapter 6, page 117) that the pH scale affords a convenient method of expressing the intensity of the alkalinity or acidity of a water. On the other hand pH gives no indication of the quantity of alkali or acid present; this must be determined by titration with standard acid or alkali respectively. A knowledge of pH value does enable us, however, to understand the kind of acidity or alkalinity present in a water. Table 78 shows the relation between pH and the kinds of acidity and alkalinity in river waters, but it must be borne in mind that these relationships may be somewhat modified in the presence of certain types of pollution.

<table>
<thead>
<tr>
<th>Approximate pH</th>
<th>Indicator changes</th>
<th>Indications</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 4.0</td>
<td>Pink to M.O.</td>
<td>Free mineral acid; possibly organic acids if in large quantity</td>
</tr>
<tr>
<td>Between 4.0 and 8.3</td>
<td>Yellow to M.O.; colourless to P.P.</td>
<td>Free carbon dioxide; possibly weak organic acids if pH between about 4.0 and 6.0; bicarbonate alkalinity</td>
</tr>
<tr>
<td>Between 8.3 and 9.4</td>
<td>Pink to P.P.; colourless to T.P.</td>
<td>Bicarbonate alkalinity Carbonate alkalinity</td>
</tr>
<tr>
<td>9.5 or over</td>
<td>Pink to P.P.; blue to T.P.</td>
<td>Carbonate alkalinity Caustic alkalinity</td>
</tr>
</tbody>
</table>

Abbreviations: M.O. = methyl orange; P.P. = phenolphthalein; T.P. = thymolphthalein.

Some acid discharges to rivers have a pH value as low as 1-2 and kier liquors may reach the high figure of 13-14 (cf. page 31), but dilution and buffer action (i.e. a high bicarbonate alkalinity figure)
Fortunately play an important part in bringing these extreme values to less harmful regions. Thus, most river waters in this country, unless grossly polluted by large volumes of acid or alkaline discharges, fall within the pH range 5.0-8.5 which is suitable for most fish (cf. page 119). Peaty moorland waters containing organic acids or those waters highly charged with carbon dioxide may fall to pH 4.5 or even lower. Such acid waters are, in general, unsuitable for fish. Pentelow states that, in general, brown trout (Salmo trutta) grow only a few inches long and weigh only a few ounces in acid waters. Nevertheless in Sutherland, Scotland, brown trout weighing as much as 4.5 lb. are found in soft waters with a pH value as low as 4.5. Many chalk streams satisfactory for the support of fish life and other aquatic organisms are alkaline towards phenolphthalein indicator (i.e. this indicator shows a pink colour) and may attain a pH of 8.5-9.0 due to the presence of dissolved calcium carbonate. Photosynthesis by algae and other plant life in sunny weather can also lead to rather high pH values in rivers; the utilization of the combined carbon dioxide in bicarbonates raises the pH value by disturbing the bicarbonate-carbonate equilibrium thus resulting in the formation of the more alkaline carbonate:

\[
2\text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O} + \text{CO}_2
\]

Indeed, Sawyer states that waters containing algae which are actively reproducing can have a pH value as high as 9.8.

According to Hewett the best waters for the support and rearing of fish life are those with pH values between 7 and 8 and having a reserve alkalinity (to methyl orange) of 100 p.p.m. (expressed as CaCO₃) which helps to prevent any sudden change in pH value. Waters with an alkalinity figure of less than 25 p.p.m. are not considered advantageous for fish since owing to their low buffering action death of fish may occur when there is a sudden fall in pH brought about by an acid discharge or by organic acids from decaying vegetation.

The significance of alkalinity in the oxidation of sewage and in the biochemical changes occurring in streams has been studied by Eckenfelder and Hoon. During oxidation of sewage there is a decrease in alkalinity caused by oxidation of carbonaceous matter to acidic substances, assimilation of ammonia by micro-organisms and oxidation of ammonia to nitric acid. Alkalinity determinations therefore give some indication of the degree of oxidation at any stage.

* A saturated solution of calcium carbonate in pure water at 15°C has a pH value of about 9.5 and contains about 13 p.p.m. of CaCO₃ but, of course, these values would be altered somewhat by the presence of other salts.
during the treatment of sewage. Streams receiving sewage effluents may undergo alkalinity changes owing to utilization of carbon dioxide, conversion of bicarbonates to carbonates by algae and other green plants, oxidation of ammonia and conversion of alkali nitrates to carbonates.

IRON

The presence of more than traces of iron in river waters generally indicates pollution by mine water (page 79) or by iron pickling wastes especially if the pH value is low and the acidity high. Waters containing iron are unsuitable for domestic or industrial purposes unless treated for its removal. Iron in solution in trade wastes really constitutes potential suspended matter since a precipitate of ferric hydroxide will form when the waste reacts with the natural alkalinity of a river water.

According to Ellis (Chapter 7, reference I, page 187) iron up to 100 p.p.m. in a river water is not specially harmful to fish or to the crustacean *Daphnia magna* (the common water flea).

CARBON DIOXIDE

Carbon dioxide can exist in streams: (a) in the combined state ('fixed carbon dioxide') as bicarbonates and carbonates of calcium and other basic ions in which form it is harmless to fish; and (b) as free carbon dioxide which is rather toxic to fish.

Ellis (Chapter 7, reference I, page 187) states that about 90 per cent of the waters of the U.S.A. containing good fish populations have a free carbon dioxide content of less than 4 p.p.m. and that where the content exceeds 6 p.p.m. there is usually some evidence of pollution. Acid wastes discharging to chalk streams can produce concentrations of carbon dioxide lethal to fish. There is, however, considerable disagreement in the literature about the toxicity threshold of carbon dioxide which apparently depends upon a number of factors such as the content of dissolved oxygen and ammonia. Alabaster and Herbert* have reported that carbon dioxide in amounts up to 30 p.p.m. was not toxic to rainbow trout within 12 hours but concentrations of 60 p.p.m. were toxic.

SUSPENDED SOLIDS, DISSOLVED SOLIDS AND TOTAL SOLIDS

The bad effects of a high content of suspended solids in effluents discharging to streams and in the stream waters themselves have been discussed in a previous chapter (see Chapter 3, page 41).
In order to limit the quantity of suspended matter passing to rivers, the Royal Commission on Sewage Disposal recommended that sewage effluents discharging to streams, where the dilution was at least 8-fold, should have a suspended solids content not exceeding 30 p.p.m. In the case of trade effluents, the corresponding figure was 40-60 p.p.m., depending on the nature of the original waste.

The dissolved solids in a stream depend in part upon the geological character of the watershed, on the rainfall, and partly on the amount of pollution taking place. A sudden rise in the content of soluble solids at a particular point on a stream often indicates pollution by an effluent.

The figure for the total solids (= suspended solids + dissolved solids) in a stream indicates the total amount of organic and mineral matter which is non-volatile at the temperature at which the determination is carried out. A sudden rise in this figure may be due to pollution and a fall may be caused by heavy rainfall. In making comparisons of B.O.D. and other determinations of river samples in different years, it is necessary to take into account the total solids figures. If these figures are roughly of the same degree of magnitude, then it can be assumed that the samples are being compared under equivalent rainfall conditions.

**Phenols**

The presence of phenols in rivers is generally caused by discharges from gas works (e.g. spent and crude gas liquors, coke-oven effluents) but many chemical waste liquors are also liable to contain phenols.

The chief effects noticeable in a river below the point of discharge of gas liquor are the presence of phenols in the river water and increases in the content of ammoniacal nitrogen and in the 4 hours permanganate value. There are also increases in the B.O.D. (not so marked as the rise in permanganate value owing to inhibition of bacterial activity by phenols and other toxic substances in the gas liquor) and pH value, the development of a considerable alkalinity to phenolphthalein indicator, and a decrease in the 4 h/3 min permanganate value ratio. These facts are illustrated by analytical data for two Lancashire rivers shown in Table 79. Naturally the magnitude of the effects of gas liquor on a stream depends upon the composition of the liquor (e.g. spent liquor will have a smaller effect than crude liquor) and upon the dilution factor.

Although laboratory experiments have shown that fish can tolerate a few p.p.m. of phenols, Kalabina states that fish are not generally found in waters containing more than 0.02 p.p.m. of
phenol. Fortunately, phenols do undergo slow biochemical change in a stream. Experiments by Ettinger and Ruchhoft\textsuperscript{7} on the persistence of phenols and cresols in polluted and unpolluted river waters in the U.S.A. have shown conclusively that the gradual disappearance of the phenols is due largely to the biochemical action of micro-organisms. Among the factors affecting the breakdown of phenols are temperature, the characteristics of the flora and fauna present, time lags in the development of the organisms, the nature and amount of the phenolic compound present and the presence of nutrient materials (e.g. nitrogen and phosphorus). Breakdown is, in general, more rapid at 20 °C than at 4 °C. Biochemical oxidation of phenols is also favoured by recent phenolic pollution (which appears to provide phenol-consuming organisms) and sewage pollution (which provides the necessary nutrients). Phenols therefore persist for much longer periods of time in unpolluted streams than in polluted streams. These authors\textsuperscript{72} also obtained rather similar results using α- and β-chlorophenols but the breakdown of these substituted phenols is much slower and appears to require the establishment of a specialized microflora.

### Table 79. Effect of gas liquors discharges on two Lancashire rivers

<table>
<thead>
<tr>
<th></th>
<th>R. Irwell</th>
<th>R. Douglas</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Above</td>
<td>Below</td>
</tr>
<tr>
<td>pH value</td>
<td>8:2</td>
<td>9:1</td>
</tr>
<tr>
<td>Permanganate value, 3 min p.p.m.</td>
<td>3:6</td>
<td>19:0</td>
</tr>
<tr>
<td>Permanganate value, 4 h p.p.m.</td>
<td>12:0</td>
<td>40:0</td>
</tr>
<tr>
<td>Alkalinity, To methyl orange, p.p.m. of CaCO(_3)</td>
<td>60</td>
<td>125</td>
</tr>
<tr>
<td>Alkalinity, To phenolphthalein, p.p.m. of CaCO(_3)</td>
<td>nil</td>
<td>50</td>
</tr>
<tr>
<td>B.O.D. (5 days, 20°C) p.p.m.</td>
<td>14:6</td>
<td>28:8</td>
</tr>
<tr>
<td>Ammoniacal nitrogen p.p.m.</td>
<td>0:8</td>
<td>17:0</td>
</tr>
<tr>
<td>Phenols (as cresol) p.p.m.</td>
<td>trace</td>
<td>1:5</td>
</tr>
</tbody>
</table>

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CHAPTER 11

PHYSICAL CHARACTERISTICS OF RIVERS

Though deep, yet clear: though gentle, yet not dull
Strong without rage, without o' reftaining full.

Sir John Denham (1615-69), "To the Thames"*

And see the rivers how they run
Through woods and meads, in shade and sun
Sometimes swift, sometimes slow.
Wave succeeding wave, they go
A various journey to the deep.
Like human life to endless sleep!

John Dyer (1707-58), "Grongar Hill"*

RAINFALL AND RUN-OFF

The rainfall map, compiled by the Ministry of Town and Country Planning and the Department of Health for Scotland from isohyets (imaginary lines joining up points with equal rainfall), and statistics contributed by the Meteorological Office show at a glance that contour lines and isohyets have a functional relationship and that the areas having a greater elevation have a greater annual rainfall. This relationship depends upon the fact that moist currents of air are forced to rise in passing over elevated ground, causing dynamic cooling and consequent rainfall. Table 80, chosen from selected stations in the British Rainfall handbook for 1950, illustrates this relationship.

To understand the cycle between rainfall and rivers it is essential, therefore, to take into account topographical considerations.

A catchment area is formed by the encircling heights to a valley. These 'water divides' can be traced from any reasonable contour map. The ordnance survey contour map, drawn to a scale of one inch equals one mile, is useful for this purpose. A line drawn between the sources of tributaries running in different directions, that is to adjoining valleys, can easily be traced and then by means of a planimeter the area of the catchment can be found. This area so measured includes all topographical features and may include a mountainous region, a hilly region and a plain or deltaic region. To each of these regions there will be a correspondingly different

* Refer to Cambridge Book of Lesser Poets.
rainfall characteristic, requiring a different technique in river control, flood protection and water storage.

The existence, as well as the direction of a range of mountains or hills, creates a variable in the equation of rainfall and run-off. A range of mountains particularly, lying at right angles to the prevailing winds and on the coast line, will produce greater amounts of rainfall than that produced over areas devoid of these topographical features. For example, annual rainfall greater than 100 in. is to be found on the western hills of America, on the southern slopes of the Himalayas and in India at the head of the Bay of Bengal. It would appear, then, that the use of empirical formulae can give fallacious results. Empirical formulae, of necessity, hope to cover these variables by means of a constant.

<table>
<thead>
<tr>
<th>Height of rain gauge above mean sea level (ft.)</th>
<th>Average rainfall per year (in.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>22</td>
</tr>
<tr>
<td>20</td>
<td>23</td>
</tr>
<tr>
<td>30</td>
<td>24.5</td>
</tr>
<tr>
<td>40</td>
<td>26.3</td>
</tr>
<tr>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>100</td>
<td>37.5</td>
</tr>
<tr>
<td>500</td>
<td>38.6</td>
</tr>
<tr>
<td>1,000</td>
<td>52.8</td>
</tr>
<tr>
<td>1,500</td>
<td>70.7</td>
</tr>
<tr>
<td>2,100</td>
<td>119.8</td>
</tr>
</tbody>
</table>

All these topographical features have a generalized connection, that is they produce orographic rainfall. This is the term used when moisture-laden air is forced to rise to higher levels, causing expansion, adiabatic cooling and rainfall. It should be mentioned that orographic rainfall can be produced over areas other than mountainous or hilly regions.

The formation of upward currents of air produces, in the form of thunderstorms, the greatest rainfall intensities. Therefore, the mountainous regions of a catchment area, or the source of a river, will, in the long run, be subjected to more severe rainfall intensities than the mouth of the river, situated at or near sea level, owing to the greater rainfall intensities experienced during a thunderstorm. This feature should not be lost sight of when designing culverts, highways and industrial reservoirs in the higher regions of a catchment area. The use, therefore, of a general rainfall curve for the design of hydrological structures could create an under-designed work in the higher regions of a catchment area.
SHAPE OF CATCHMENT AREA

The shape of a catchment area and again its orientation, is another factor in the rainfall and run-off equation. The regime of a river depends upon the shape of its catchment area.

A long narrow catchment area will not maintain as plentiful a supply of water as a broad area, also evaporation will be greater in a catchment area having a southern aspect than that having a northern aspect. Snow will predominate in a catchment area having its mountainous region to the south. Here again a variable is introduced into the rainfall and run-off equation when applied to two catchment areas of different shape but otherwise equal in all respects. The constant factor that can be applied to each area individually is that stated in 1932 by LeRoy K. Sherman (U.S.A.) that, 'For all unit storms regardless of their intensity the period of surface run off is approximately the same.'

SIZE OF CATCHMENT AREA

The size of catchment area plays an important part in the design of hydrological structures. If small areas are being considered, greater rainfall intensities should be used in the run-off equation than when considering larger areas. This is due to the fact that rainfall intensities decrease from the centre of a storm outwards.

As shown by Dr. J. Glaspoole in a paper read before the Institution of Civil Engineers in December 1929, this reduction at the outer edge of the storm may be 35 per cent of the intensity at the centre of a storm when considering an area of 100 square miles.

GEOLoGY

The geological formation of a catchment area has an influence upon the amount of rainfall that finds its way into a river, or, expressed more concisely, the run-off coefficient will vary according to the geological formation.

Most rivers emerge as springs in the higher rocky regions. Springs are due to the intervention of impervious strata which holds up the water and enables it to reappear at the surface. Owing to fissures in the rock it is possible to have large amounts of water stored underground. This water may overflow into an adjoining catchment area, thus causing a decreased run-off coefficient for the one catchment area and an increased coefficient for the other.

The velocity of a river is greatest at its steepest gradient, which will usually be found at its source in the higher regions, and least at its...
mouth where flatter gradients are to be found. As the capacity of the river to carry suspended solids depends upon the velocity of the water (and this capacity varies as the sixth power of the velocity) a greater abrading power will be realized in the higher regions of the river. As the velocity decreases at the mouth of the river the velocity will not be sufficient to carry the sand and gravel and a tendency to shoal will occur. In other words the river will tend to reduce its gradient and produce some kind of exponential curve along its longitudinal section.

RIVER GAUGING

To obtain a dilution factor, with regard to pollution, it is necessary to know the discharge of the river, stream or brook at the point of sampling. This discharge can be expressed by the equation \( Q = AV \); where \( Q \) is discharge in cubic feet per second, or cusecs, \( A \) = sectional area in square feet of the channel from water surface to channel bed, \( V \) = velocity of stream in feet per second. If the discharge \( Q' \) is required in million gallons a day the equation becomes \( Q' = 0.538 (AV) \).

The sectional area is easily obtained in the case of a brook by stretching a tape across the water surface and taking soundings at equal intervals; the length of the intervals depending upon the total width of the brook. In the case of a shallow brook these soundings can be obtained by wading; the depth of water being taken at, say, every 5 ft. from one bank. Elementary mensuration or the use of Simpson's rule will then give the required area. In deeper water a boat or bridge will have to be used to obtain the soundings.

The measurement of the velocity of a brook will present a little more trouble. In the case of a very shallow brook, say 12 in. or less at its deepest point and some 15 ft. wide, the surface velocity, obtained by timing a float over a measured distance, will give an approximation to the correct result. It should be remembered, however, that the velocity will not be the same at all points, a retardation in the velocity taking place at each bank and at the under surface. Therefore, the surface velocity if measured in the centre will give a discharge greater than the actual.

If more accurate results are required when dealing with a small brook, the discharge of which is, say, one million gallons a day or thereabouts, a little more trouble and time is required.

Providing all the water can be contained between walls, for example retaining walls or bridge abutments, a steel plate with a rectangular opening or with a 90° V-notch can be placed across the stream, and the level of water on the crest of the rectangular opening or above the apex of the V-notch can be obtained by careful
measurements; or if fluctuations in flow are required, a portable recorder can be fixed so that a trace over any particular time period can be obtained. The height of water is then converted to discharge quantities by means of a weir formula, such as

\[ Q = 3.33 \times b \times h \] for the rectangular opening,

or \[ Q = 0.003 + 0.005 \times h^{0.5} \] for the 90° V-notch,

where \( Q \) = discharge in cubic feet per second, \( b \) = width of weir in feet, and \( h \) = height of water in feet on the rectangular opening and in inches on the V-notch. The plate must be level and all the water must be made to pass over the rectangular opening or V-notch. The measurement of the depth of water (\( h \)) must be taken a little way upstream of the plate, say some 5 ft.

The velocity can also be obtained by means of a current-meter. One type of instrument consists of a series of anemometer cups revolving on a vertical axis, an electric circuit being made at each revolution, the number of revolutions being recorded on a counter or aurally counted through headphones and their frequency timed with a stopwatch. The instrument should be frequently checked so that there is no deviation from the original rating curve. This curve gives the velocity in feet per second against the revolutions per second.

To gauge the discharge of a river a rope or wire is stretched tightly across it and divided into equal divisions by marks, at which vertical sections of the velocity distribution are to be measured. After measuring the depth of the vertical the most accurate method is to measure the velocity at a number of points in that vertical, if there is a sufficient depth of water to do so, and to plot these as 'velocity cross-sections', extrapolating for the surface and bottom velocities which cannot, of course, be measured. The areas of these curves are then taken out with a planimeter (or by Simpson's rule) and are treated as equidistant cross-sectional areas of a solid whose volume is the discharge. Less accurate methods are to take a single reading of the velocity, \( v_h \), at half depth, \( d \), on each vertical and take the area as 0.96 \( v_h \) \( d \), or to take the velocity at 0.6 \( d \) (or the average of the velocities at 0.2 \( d \) and 0.8 \( d \)) as the mean velocity, \( \bar{v} \), so that the area = \( \bar{v} \times d \).

In some cases it will only be possible to take one current-meter reading on each ordinate when dealing with small streams. In this case, the procedure shown in Table 81 might be adopted.

It will be noticed here that a mean velocity as shown in column G is obtained for each section as \( Q = \bar{A} \bar{V} \), the total \( Q \) is given by the summation of column H, and the total area is given by the summation of column D. The mean velocity over the whole section will, therefore, equal 25.71/47.40 which equals 0.54 ft./sec.
**PHYSICAL CHARACTERISTICS OF RIVERS**

Table 81. Calculation of discharge of a small stream from current meter readings. 
Mersey River Board Gauging and Survey Department, River Alt, Pollution Point E, 
Alt Bridge, 24 August 1955

<table>
<thead>
<tr>
<th>A.</th>
<th>B.</th>
<th>C.</th>
<th>D.</th>
<th>E.</th>
<th>F.</th>
<th>G.</th>
<th>H.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Revs.</td>
<td>Area of section</td>
<td>Revs. of current meter</td>
<td>Mean velocity at depth of reading</td>
<td>C.</td>
<td>Sec.</td>
<td>Discharge in acre ft.</td>
<td></td>
</tr>
<tr>
<td>ft.</td>
<td>ft.</td>
<td>sec</td>
<td>ft.</td>
<td>ft.</td>
<td>sec</td>
<td>ft.</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>5</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0.285</td>
<td>1.12</td>
</tr>
<tr>
<td>5</td>
<td>5</td>
<td>1.58</td>
<td>8.95</td>
<td>15</td>
<td>64</td>
<td>64</td>
<td>0.605</td>
</tr>
<tr>
<td>10</td>
<td>5</td>
<td>2.00</td>
<td>10.63</td>
<td>15</td>
<td>56</td>
<td>56</td>
<td>0.645</td>
</tr>
<tr>
<td>15</td>
<td>5</td>
<td>2.25</td>
<td>10.62</td>
<td>15</td>
<td>54</td>
<td>56</td>
<td>0.635</td>
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<td>2.00</td>
<td>8.75</td>
<td>15</td>
<td>57</td>
<td>59</td>
<td>0.62</td>
</tr>
<tr>
<td>25</td>
<td>5</td>
<td>1.50</td>
<td>8.40</td>
<td>8</td>
<td>47</td>
<td>3.43</td>
<td>0.525</td>
</tr>
<tr>
<td>31</td>
<td>6</td>
<td>4.50</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>0</td>
<td>0.215</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B.</th>
<th>C.</th>
<th>D.</th>
<th>E.</th>
<th>F.</th>
<th>G.</th>
<th>H.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ft.</td>
<td>ft.</td>
<td>rev</td>
<td>sec</td>
<td>ft.</td>
<td>sec</td>
<td>acre ft.</td>
</tr>
<tr>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
<td>--------</td>
</tr>
<tr>
<td>47.40</td>
<td>50</td>
<td>0</td>
<td>60</td>
<td>0</td>
<td>0.540</td>
<td>25.71</td>
</tr>
</tbody>
</table>

**COMPENSATION WATER**

The construction of a reservoir alters the natural regime of a river. To prevent undue disturbance to the users of the river water downstream of the reservoir and to maintain a reasonable semblance of the original regime, the water authority constructing the reservoir is compelled by statutory legislation to maintain a certain flow of water down the river for all times. This quantity of water is known as compensation water.

The quantity that the water authority must allow to flow down the river is fixed by law and is a proportionate part of the run-off of the catchment area of the reservoir. A general figure is ¼ of the available yield of the catchment (especially in an industrial area) but other ratios are sometimes allowed. It would appear that each individual case must be dealt with on its own merits. A river flowing through an industrial area would require as a general rule a greater amount of compensation water than one flowing through an agricultural area as there is a greater need for dilution of industrial effluents.
ASPECTS OF RIVER POLLUTION

DRY WEATHER FLOW AND MEAN DAILY FLOW

The dry weather flow of a river plays an important part in pollution problems. The definition of dry weather flow is far from precise at the moment. A logical definition of the absolute dry weather flow in industrial areas can be taken as the sum of the effluents from factories, sewage works, etc. (after a suitable period of dry weather), and compensation water from reservoirs plus an empirical ground water discharge, but, as this condition is most infrequent, it would appear that a definition termed the 'standard flow' (see page 416) would be of more use in pollution problems.

Once a fair and reasonable figure has been established as the standard flow (q.v.) it is often convenient to express the flow of the river as a ratio, obtained by dividing the mean daily flow by the standard flow. By using the standard flow it is possible to have ratios less than unity, thus covering the few occasions when the flow may be abnormally low.

The mean daily flow is obtained from a continuous recording

![Figure 27. River Mersey. Histogram showing mean daily flows at Irham Weir for the period 1 October 1943 to 30 September 1954 (i.e. 3,287 occurrences)
recorder chart, either by obtaining the area under the curve by planimeter, or by analysing the information obtained from weekly charts.

In the case of the Mersey River Board the analysis for uncalibrated charts is carried out as follows. By the use of a calculating machine the mean daily flow is calculated by using Simpson's rule, the ordinates being the river level at three hourly intervals converted to cusecs from a stage discharge curve made up from current meter gaugings. The following table shows a completed analysis:

<table>
<thead>
<tr>
<th>Date</th>
<th>Mean daily discharge</th>
</tr>
</thead>
<tbody>
<tr>
<td>09.00</td>
<td>20.3</td>
</tr>
<tr>
<td>12.00</td>
<td>24.6</td>
</tr>
<tr>
<td>15.00</td>
<td>47.0</td>
</tr>
<tr>
<td>18.00</td>
<td>71.0</td>
</tr>
<tr>
<td>21.00</td>
<td>47.0</td>
</tr>
<tr>
<td>24.00</td>
<td>39.0</td>
</tr>
<tr>
<td>03.00</td>
<td>39.0</td>
</tr>
<tr>
<td>06.00</td>
<td>39.0</td>
</tr>
</tbody>
</table>

The mean daily discharge is obtained by multiplying the discharge at 09:00 hours by 1, 12:00 by 4, 15:00 by 2, 18:00 by 4, 21:00 by 2, 24:00 by 4, 03:00 by 2, 06:00 by 4, and 09:00 by 1, and dividing the sum of the products by 24 providing the chart is a seven-day chart.

Returning now to the standard flow; Table 82 gives the mean daily flow of the River Mersey for the nine-year period 1 October 1945 to 30 September 1954. This distribution is also shown plotted in Figure 27 and it will be noted that it is a skew distribution, as so many things occurring in nature are.

The accumulation of hydrological data such as daily rain and river gauging is of no practical use unless the records are analysed and presented in such a form that the relevant points are brought out and a quick understanding of the rainfall and run-off conditions are obtainable. At the same time over analysis should be avoided as this may prevent one seeing the 'wood for the trees'.

The relevant points in connection with river gauging records from
the statistical point of view can perhaps be summarized by the mean, mode and standard deviation. The mean is not simply the arithmetical mean but a weighted mean as described later. The mode is the frequency carrying the greatest number of occurrences; for example, we notice in Figure 27 that the mode lies between the 100 and 200 cusec class. The standard deviation gives a measure of dispersion about the mean.

Table 42. Distribution of 3,287 mean daily flows and cumulative totals and per cent.

<table>
<thead>
<tr>
<th>Cusec class mid-point</th>
<th>Frequency</th>
<th>Cumulative total</th>
<th>Cumulative per cent</th>
<th>Cusec class mid-point</th>
<th>Frequency</th>
<th>Cumulative total</th>
<th>Cumulative per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>85</td>
<td>85</td>
<td>2.59</td>
<td>3283</td>
<td>99.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>807</td>
<td>582</td>
<td>29.60</td>
<td>4450</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>809</td>
<td>1791</td>
<td>54.49</td>
<td>4550</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>350</td>
<td>489</td>
<td>2280</td>
<td>69.36</td>
<td>4650</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>450</td>
<td>240</td>
<td>2520</td>
<td>76.67</td>
<td>4750</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>169</td>
<td>2669</td>
<td>81.61</td>
<td>4850</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>650</td>
<td>103</td>
<td>2792</td>
<td>84.94</td>
<td>4950</td>
<td>99.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>750</td>
<td>79</td>
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<td>6350</td>
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<td>6650</td>
<td>99.85</td>
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</tr>
<tr>
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<td>6</td>
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<td>99.94</td>
<td>6750</td>
<td>99.85</td>
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<td>3550</td>
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<td>8050</td>
<td>99.97</td>
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<td></td>
<td>3286</td>
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<td>8250</td>
<td>99.97</td>
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<td>99.82</td>
<td>8350</td>
<td>99.97</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>1</td>
<td>3282</td>
<td>99.85</td>
<td>8450</td>
<td>99.97</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4250</td>
<td>1</td>
<td>3283</td>
<td>99.88</td>
<td>8550</td>
<td>99.97</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| 4350                  | 1         | 3284            | 99.91               | 8650                  | 99.97     |                 |                     |

| 4450                  | 1         | 3285            | 99.94               | 8750                  | 99.97     |                 |                     |

| 4550                  | 1         | 3286            | 99.97               | 8850                  | 99.97     |                 |                     |

| 4650                  | 1         | 3287            | 100.00              | 8950                  | 99.97     |                 |                     |
Table 82, column 2, shows the 9 years summation of mean daily flows of the River Mersey at Irland Weir. Mean daily flows, as can be noted, are grouped into classes of 100 cusec, that is all flows during the nine years between 0 to 100 cusec are grouped into the 50 cusec class, the mid-point 50 cusec being shown in column 1. All flows between 101 cusec and 200 cusec are grouped under the 150 cusec class and so on. Column 3 shows the cumulative totals and column 4 shows the cumulative per cent. If the cumulative per cents are plotted on probability paper with the cusec classes as abscissae and per cents as ordinates a curve is produced as shown in Figure 28. This curve resembles a logarithmic curve; since the derivative of log \( x \) is \( 1/x \), the slope of the curve is steep for small values of \( x \) and less steep for large values of \( x \). If, therefore, a new diagram is plotted on logarithmic probability paper, as shown in Figure 29, the points should lie about a straight line. We may, therefore, consider the logarithm of the cusec classes to be normally distributed.

Having established the fact that the distribution is similar to a logarithmic distribution curve the frequencies are retabulated.
Figure 29. Fractile diagram. River Mersey, Irland Weir. Mean daily flows. 1 October 1945 to 30 September 1954

Figure 30. Histogram. River Mersey, Irland Weir. Mean daily flows. 1 October 1945 to 30 September 1954
PHYSICAL CHARACTERISTICS OF RIVERS

according to the logarithm of the cusec class. Table 83, columns 1 and 2, shows this redistribution and Figure 30 also shows the retabulation with the logarithm of the cusec class as abscissa. From this diagram it will be seen that the distribution is no longer skew.

The next step is to find the mean and standard deviation of the distribution given in columns 1 and 2 of Table 83.

The arithmetic mean as given by

$$\bar{x} = \frac{\sum_{i=1}^{n} f_i x_i}{n}$$

in this case would not be truly representative as no weight would be given to the frequency of flows against each cusec class.

The mean is found by taking, as it were, moments about some specific point. Table 83, column 3, shows that the log 2.3 cusec class has been arbitrarily chosen as a point about which moments have been taken, log cusec classes below this point having negative values and log cusec classes above this point having positive values. The only reason in arbitrarily placing the zero against the log 2.3 cusec class is to reduce the magnitude of the figures to be worked with, otherwise the zero can be placed at the beginning of the table, i.e. at the log 1.5 cusec class or any other point.

The mean is now found by

$$\bar{x} = \frac{\sum (f_i x_i)}{n}$$

The figure produced by the equation assumes that the log scale and
x scale are of equivalent value. In the case quoted, the log scale rises in increments of 0.2 whereas the x scale varies by unit integers. Therefore, to convert the mean x value to cusecs

\[
\frac{f_1 + f_2 + \ldots + f_n}{n}
\]

must be multiplied by 0.2, i.e. the ratio between the two scales. We can write that the log of the mean of the logarithmic distribution

\[
\log x = 2.3026 \log e = 2.3026 \cdot \frac{1}{0.4343}
\]

Although the logarithmic mean flow has now been obtained, the figure by itself means little. For example, 9, 10, 11 and 0, 10, 20 both have the same mean, although there is a wider divergence of the extreme values on one set of figures than the other. To find this measure of dispersion, the standard deviation is used.

To obtain the standard deviation another column is formed in Table 83 from the previous figures and is the product \( jx^2 \), or the figures used for obtaining the 'mean daily flow' are simply multiplied by the number corresponding to the working scale. The total of this column will be \( \sum jx^2 \) and the standard deviation is obtained from

\[
\sqrt{\frac{\sum jx^2 - (\frac{\sum jx}{n})^2}{n-1}}
\]

giving the measure on our working scale which when converted to the cusec scale becomes

\[
\sqrt{\left(11,718 - \frac{2,982^2}{3,287}\right) \frac{3,287}{3,286} 0.2}
\]

= 0.3312

As already pointed out, the mode is the cusec class having the greatest frequency and this class is defined as the 'standard flow' for discharges at Irlam Weir on the River Mersey. This is the discharge figure to which all dilution factors in pollution problems could be compared. The evaluation of this figure based on a formula due to Hald \(^ {15} \) is obtained by

\[
\log x = 2.4814 - 2.3026 \log e = 0.3312
\]

= 170 cusecs

In the above equation \( \log x \) is the mode, 2.4814 is the mean of the logarithmic distribution, 2.3026 is the reciprocal of \( \log e \) or 1/0.4343,
and 0.3312 is the standard deviation of the logarithmic distribution. The mean can also be calculated as follows:

\[ 2.4814 + (1.1513 \times 0.3312^2) \]

= 405 cusecs

In the above equation 2.4814 is the mean of the logarithmic distribution, 1.1513 is half the reciprocal of \( \log e \) or \( 1/2 \times 0.4343 \), 0.3312 is the standard deviation of the logarithmic distribution.

**REFERENCES**

3. BRUNT, D., *Physical and Dynamical Meteorology*. Cambridge University Press, 1941
8. SCOBIE, R. F. ( Brig.-Gen.), *Geology for Engineers*. Bell and Sons, London, 1938
CHAPTER 12
ABATEMENT OF POLLUTION.
I. SEWAGE DISPOSAL AND PURIFICATION

The object of sewage disposal is not to produce an effluent which is as good as drinking water, nor even necessarily one in which fish and other aquatic fauna and flora can live. It is to produce an effluent which can be discharged into an adjacent stream without creating objectionable conditions.

A. Key. Gas works effluents and ammonia.

INTRODUCTION

It has been shown in previous chapters (see Chapters 3 and 4) that the sewage discharged from villages, towns and cities constitutes one of the main sources of pollution of our rivers and watercourses. One of the most important steps to be taken towards the abatement of this pollution, therefore, lies in the direction of efficient sewage disposal and purification. In this chapter, a review of the methods available for this purpose will be given, but for further details, especially in connection with the design and operation of sewage disposal works, the reader is referred to the special books on the subject.

Sewage from non-industrial towns generally consists of purely domestic sewage, that is wastes from kitchens, bathrooms, washbasins, and lavatories. The sewage arriving at the sewage works may be fresh (i.e. it will still have some dissolved oxygen present), it may be stale (i.e. the dissolved oxygen will have become exhausted), or, especially in hot climates or if it has travelled through very long lengths of sewer, it may be septic owing to the development of anaerobic organisms which reduce sulphates and organic sulphur compounds to hydrogen sulphide. Septic sewage has an odour of hydrogen sulphide, is dark-coloured, has a high 3-minutes permanganate value and is more difficult to treat than fresh or stale sewage.

Sewage from industrial towns generally contains varying proportions of trade wastes from industrial premises. Since the passing of the Public Health (Drainage of Trade Premises) Act, 1937, most domestic sewage can also arise from (a) towns whose industries mainly carry out dry processes, and (b) industrial towns whose wastes are not discharged to the sewers.
industrial towns have accepted increasing volumes of trade wastes into the sewers. Although, in general, this makes the sewage more difficult and more costly to purify and may involve considerable extensions to the sewage works and better facilities for sludge disposal, the methods used for dealing with an industrial sewage are essentially similar to those used for a purely domestic sewage. Although the 1937 Act confers the right on the manufacturer to discharge his waste waters to the public sewers, there are naturally certain conditions and safeguards. Thus, the local authority may refuse to admit certain harmful wastes and may require the trader to carry out certain pre-treatment to prevent damage to the sewerage system. Many authorities now refuse to admit to their sewers trade wastes containing sulphides since there have been fatalities to men working in the sewers due to evolution of poisonous hydrogen sulphide by interaction of the sulphides and acidic wastes. Many of the important sewage treatment processes make use of bacterial action so care must be taken to see that the concentration of toxic substances is not so high as to involve any marked interference with bacterial activity. For instance, electroplating wastes may contain such bacterial poisons as copper, chromate, cadmium, nickel and cyanides; most of these substances cause interference with sewage treatment processes when present in sewage to the extent of about 1-2 p.p.m.

THE STRENGTH OF SEWAGE

Sewages from different towns show marked variations in the amount of organic matter present and are said to differ in strength. The strength is generally regarded as the amount of oxygen required to oxidize the oxidizable matter in a specified volume of sewage.* Since the strength is dependent upon the quantity of oxidizable organic matter present, the estimation of strength can be carried out by determining the amount of oxygen required for the complete oxidation of this organic matter. In practice this is not easy to do and so the assessment of strength is usually based on such tests as B.O.D., ammoniacal and organic nitrogen, permanganate oxygen absorption, oxygen taken up from potassium dichromate, and so on. McGowan* in a Royal Commission report suggested the following alternative formulae for calculating the strength of a sewage (i.e. the number of parts of oxygen by weight taken up by

* The ease or difficulty with which a sewage can be treated by biological methods and therefore the capacity of the purification plant required are not necessarily related to the strength of the sewage but depend upon the nature of the substances present and their toxicity to micro-organisms responsible for the purification.
100,000 parts of the sample during oxidation) based upon determinations of the oxygen absorbed by strong (N/8) potassium permanganate in 4 hours at 27°C in acid solution, the ammoniacal nitrogen, and the organic nitrogen (all expressed as was customary in those days in parts per 100,000, i.e. mg per 100 ml.):

1. \((\text{Ammoniacal nitrogen} + \text{organic nitrogen}) \times 4.5 + (\text{permanganate value} \times 6.5)\).
2. \((\text{Ammoniacal nitrogen} + \text{organic nitrogen}) \times 3 + (\text{permanganate value} \times 8)\).
3. \((\text{Ammoniacal nitrogen} \times 4.5) + (\text{permanganate value} \times 8)\).

These three formulae, which are strictly valid only for domestic sewages, all give approximately the same result and a rough figure for strength can also be obtained by multiplying the N/8 permanganate figure by 10. On the basis of strength, McGowan classified sewages as follows:

<table>
<thead>
<tr>
<th>Sewage</th>
<th>McGowan strength figure (parts per 100,000)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak</td>
<td>60–100</td>
</tr>
<tr>
<td>Average</td>
<td>100–175</td>
</tr>
<tr>
<td>Strong</td>
<td>175 or over</td>
</tr>
</tbody>
</table>

As pointed out by the present author, a practical disadvantage of estimating strength by the use of the McGowan formula is that most sewage works laboratories nowadays determine albuminoid nitrogen (instead of organic nitrogen) and the N/80 permanganate value (rather than the N/8 figure). The conversion to the corresponding organic nitrogen and N/8 permanganate values has to be carried out by more or less dubious factors which do not necessarily apply to every sewage. It is often assumed that the factor 1.6 can be used to convert an N/80 permanganate value to an N/8 value but the various sewages examined by the author gave an average N/80:N/8 ratio which varied from 1.17 to 1.43. In view, therefore, of the many disadvantages attaching to the use of the McGowan method of estimating the strength of sewage, the tendency in this country today is to use either B.O.D. or the 4 hours N/80 permanganate value for assessing sewage strength.

In the U.S.A. the 5-day B.O.D. is generally used as a measure of sewage strength but, as pointed out in Chapter 10, it is not always reliable and can give misleading results in the presence of certain inhibitory trade wastes. For this reason, the determination of the oxygen consumed from potassium dichromate is beginning to find favour in America where it is termed Chemical Oxygen Demand or C.O.D.

Escritt, on the basis of tests carried out on 21 sewages, found the
The following relationship between the McGowan strength figures and B.O.D.:

<table>
<thead>
<tr>
<th>McGowan strength figure (parts per 100,000)</th>
<th>5-day B.O.D. (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak sewage 60</td>
<td>210</td>
</tr>
<tr>
<td>Average sewage 100</td>
<td>350</td>
</tr>
<tr>
<td>Strong sewage 170</td>
<td>600</td>
</tr>
</tbody>
</table>

It must be emphasized, however, that this relationship is only an approximate one which might easily be upset by the presence of certain trade wastes.

In this country, the N/80 permanganate value determined in dilute sulphuric acid solution for a period of 4 hours at 27°C is generally regarded as providing a rough measure of the strength of a sewage, and the following easily remembered classification has been suggested by Keys:

<table>
<thead>
<tr>
<th>Domestic sewage</th>
<th>4 hours N/80 permanganate value (27°C) (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak 50</td>
<td></td>
</tr>
<tr>
<td>Average 100</td>
<td></td>
</tr>
<tr>
<td>Strong 150</td>
<td></td>
</tr>
</tbody>
</table>

Hence if 1,000 gal. of a trade waste with a 4 hours permanganate value of 2,000 p.p.m. is admitted to the sewers, the waste will be 20 times as strong as an average domestic sewage and will be roughly equivalent to 1,000 × 20 = 20,000 gal. of average domestic sewage.

Among the important factors which determine the strength of a sewage are the type of sewerage system (i.e. whether combined, separate, or partially separate), the amount of infiltration water leaking into the sewers, the daily water consumption per head of population, the food and other habits of the population, and the amount and character of the industrial wastes present. It is obvious that where the sewerage system is a combined one taking all the storm water, the sewage will be relatively weak during periods of heavy rainfall and relatively strong during prolonged dry weather. In this country, where the average water consumption in towns is only in the region of 40 gal. per head per day, the sewages are markedly stronger, more colloidal in character, and considerably more difficult to deal with than sewages in the U.S.A. where the average water consumption may be as much as 100-200 gal. per head per day. Trade wastes have a big influence on the strength of a sewage and on its amenability to treatment. Thus, the large quantities of industrial wastes discharging to the sewers of Bradford, Yorkshire (the largest wool-scouring centre in the world), make the
sewage one of the strongest and most difficult to treat in the whole of England; 50 per cent consists of trade effluents chiefly from wool-scouring plants and dye-works. This sewage, whose 4 hours permanganate value over a period of one year averaged 228 p.p.m., was at one time considered to be untreatable on account of the large proportion of emulsified wool grease. Precipitation with sulphuric acid, however, removes the bulk of this grease and the settled tank effluent is then amenable to treatment on percolating filters after its acidity has been somewhat reduced by admixture with a slightly alkaline domestic sewage. The Klipspruit works of Johannesburg, S. Africa (the largest of several sewage works serving that city) has the dubious distinction of having one of the strongest and most greasy sewages in the world, with a 4 hours permanganate value of about 199 p.p.m. according to HAMLIN. This high strength is due to a combination of several adverse circumstances; the sewerage system is separate and not combined and so does not have the advantage of dilution by rain water, the water consumption is comparatively low, the water is hard which necessitates the use of large amounts of soap, and finally all the trade wastes in the city go to this one works.

In the U.S.A., the strength of trade wastes admitted to the sewers is often expressed in terms of the equivalent population. An American domestic sewage in dry weather has a 5-day B.O.D. ranging from 0·14 to 0·20 lb. per head of population per day—the average can be taken to be 0·17 lb. Hence the population equivalent of an industrial sewage or of a trade waste is given by the expression:

\[
\text{Population equivalent (U.S.A.)} = \frac{\text{lb. of 5-day B.O.D. contributed per day by industrial sewage or waste}}{\text{lb. of 5-day B.O.D. contributed by domestic sewage per day per head of population}}
\]

\[
= \frac{\text{lb. of 5-day B.O.D. contributed per day by industrial sewage or waste}}{0\cdot17}
\]

\[
= \frac{5\text{-day B.O.D. in p.p.m.} \times \text{flow in m.g.d.}}{8\cdot34}
\]

\[
= \frac{6\cdot17}{8\cdot34}
\]

(Since 1 U.S.A. gallon of water weighs 8·34 lb.)

SOUTHGATE has calculated that, assuming the average volume of domestic sewage in Britain is 30 gal. per head per day with a 5-day B.O.D. of 400 p.p.m., the corresponding British 5-day per capita B.O.D. is 0·12 lb. and so for this country the population equivalent of an industrial sewage is given by the expression:
Population equivalent (British)

\[
\text{5-day B.O.D. in p.p.m. } \times \text{flow in m.g.d.} \times 10^{-12}
\]

(Since 1 imperial gallon of water weighs 10 lb.)

The rate of flow of sewage arriving at a disposal works varies from hour to hour. In the case of domestic sewage in dry weather, the minimum rate of flow is generally in the early morning (about 1 a.m. to 6 a.m.) when the sewage is usually at its weakest whilst the maximum rate of flow usually occurs around midday (about 11 a.m. to 1 p.m.) when the strength of the sewage also reaches a maximum. Deviations from these times may, however, be caused by rainfall, trade effluent discharges, infiltration water leaking into the sewers, sewer gradients, and the length of the outfall sewer.

PRELIMINARY TREATMENT OF SEWAGE

Sewage is generally given some preliminary treatment in order to remove the coarser solid materials and gritty matter.

The sewage is first passed through bar screens with openings about \( \frac{1}{4} \) in. to remove such coarse materials as rags, paper, faecal matter, etc. It then flows through detritus tanks (called 'grit chambers' in the U.S.A.) whose function is to remove abrasive gritty matter having a high mineral content, such as sand, gravel, cinders, etc.\(^*\) The velocity of flow through these tanks must be sufficiently high (usually about 1 ft./sec) to enable the grit to settle in a clear condition as free as possible from organic matter. Many modern sewage works have detritus tanks provided with mechanical devices for removing the detritus. The solids in the old type of detritus tank (usually removed by hand or by grab bucket) often contain much organic matter and the disposal of this putrescible product presents a problem. In the Dorr Detritor, a new principle is introduced involving the washing of the grit. A tank is provided of sufficient size to collect all the detritus under conditions of maximum sewage flow and there is a scraping device which sweeps all the solids into a cleaning mechanism which pushes the detritus up an inclined plane and at the same time thoroughly washes it and removes light organic material (which passes on to the sedimentation tanks) while the grit is clean enough to use on paths or as a fill.

When the sewage contains abnormally large amounts of oil and grease, special skimming tanks are sometimes provided for the purpose of removing as much floating oil and grease as possible with or without the use of such aids as aeration for short periods\(^1\),

\(^*\) The sequence of screening and grit removal is reversed at some sewage works.
chlorination, and vacuum flotation. Walker claims that pre-aeration of sewage makes the sewage much easier to treat subsequently by biological processes, and particularly good results are obtained with stale and septic sewages. The grease removed by skimming has often a considerable commercial value.

**EARLY METHODS OF SEWAGE DISPOSAL AND TREATMENT**

**Disposal to soakaway**

The sewage is allowed to flow into a shaft or pit from which it percolates through the soil and undergoes purification. This method may lead to pollution of underground water supplies and should only be used where no other method is suitable or available. Moreover, it can only be used for small flows and where the subsoil is porous.

**Disposal by dilution**

Although much pollution has been caused in the past by the uncontrolled discharge of crude sewage to rivers, nevertheless, subject to certain safeguards, the method of disposal by dilution with large volumes of river water—thus making use of the natural purification capacity of the stream—can under certain circumstances give satisfactory results. The chief limiting factor in the purification of sewage by the dilution method is that fully aerated river water contains only comparatively small amounts of oxygen (e.g. at 14°C only about 10 p.p.m. of dissolved oxygen) whereas the biochemical oxygen demand of sewage is in the region of 30-50 times this amount. Hence, the complete oxidation of sewage by disposal and dilution in a river might easily require a distance of 15-30 miles of travel.

The Royal Commission on Sewage Disposal recommended that crude sewage could be discharged safely to a river provided that the dilution was over 500 volumes and that screens and detention tanks were provided to remove floating materials and grit. Also, if the sewage were given settlement in tanks to remove suspended solids, then dilution with 300-500 volumes of clean river water would be sufficient. It is, however, rare on the comparatively small inland streams in this country to find suitable local conditions, such as adequate dilution and sufficient stream velocity, to enable the dilution method to give satisfactory results. In estuarial waters where the method has been in use for a long time the result has been gross pollution and in many cases destruction of fisheries, probably because the polluting matter has moved to and fro with the tides instead of being quickly carried out to sea. In the U.S.A., where the rivers are so much larger, disposal of sewage by dilution is quite
common, but even there it has been abandoned in some cases (e.g. New York, Boston) because of the gross pollution produced, and proper treatment plants have been set up. An ingenious application of the dilution method has been made by Imhoff\(^{19}\) in the densely populated Ruhr valley in Germany. Here a series of large impounding or artificial lakes have been constructed to receive the mixture of river water and settled sewage from the various tributaries of the River Ruhr. These reservoirs have the effect of virtually shortening the stretch of river required for natural self-purification and really replace and render unnecessary the normal biological processes of sewage treatment. They have the further advantages of affording opportunities not only for recreation, bathing and boating but also for the development of water power.

**Land treatment**

One of the oldest methods of disposal of sewage, and one that can be combined with the growing of crops, is treatment on land. Indeed, Reynouard\(^ {20} \) records that Bünzlau in Silesia had a public sewage plant making use of land treatment as early as 1543. Disposal on land can be carried out either by irrigation over a large area of land (broad irrigation) or alternatively by filtration through a porous loamy soil (intermittent downward filtration) which requires a smaller area of land than does irrigation. In either case the sewage should be screened and settled before application to land. The changes taking place during filtration through the ground are brought about by soil micro-organisms and are similar to those occurring when sewage is oxidized aerobically on percolating filters or by activated sludge. The sewage has an appreciable fertilizing value, since according to Veatch\(^ {21} \) it contains approximately 20 p.p.m. of nitrogen, 6 p.p.m. of phosphoric acid (P\(_2\)O\(_5\)) and 4 p.p.m. of potash (K\(_2\)O).

Owing to the large areas of land required, the high cost of land near towns and cities, the occurrence of unpleasant smells especially with strong sewages, the possibility of causing pollution to underground water supplies, and a tendency for the land to become septic or ‘sewage sick’ (thus necessitating a long rest and dressing with lime to aid recovery), sewage farms utilizing land treatment have now been largely superseded in this country by modern treatment plants using biological filters or activated sludge. Land treatment is now confined either to very small communities or to cases where a treated effluent requires a final ‘polishing’ method. On the Continent, especially in Germany, land treatment still finds fairly extensive application notably for the treatment of Berlin sewage. The method is also still practised in the arid regions in the southwest of the U.S.A. where land is cheap and easily available, streams
are small or non-existent, and conservation of every gallon of water for crops is essential.

The area of land required for the treatment of sewage depends upon a number of factors such as the strength of the sewage, the nature of the soil, the extent to which crops are grown, and whether irrigation or downward filtration is practised. The Royal Commission in its 5th Report [22] stated that sewage after preliminary treatment can be dealt with at a rate of filtration of up to 30,000 gal. per acre per day on the very best soils (corresponding with the sewage from 1,000 persons, assuming 30 gal. of sewage per head of population per day).

Sedimentation

The removal of suspended solids (or strictly speaking 'settleable solids') from sewage by settlement in tanks is one of the most important methods of treatment. In early times, the tanks used were of the 'fill and draw' type but nowadays continuous flow tanks are employed and in the more modern type of tank the sludge formed is continuously removed by mechanical scrapers. The moisture content of the sludge removed ('sedimentation tank sludge' or 'primary sludge') should be about 95 per cent or less.

The Royal Commission on Sewage Disposal in their 5th Report [22] recommended that sedimentation tanks should deal with up to 3 x D.W.F. of sewage and the detention period suggested was from 10-15 hours at D.W.F., i.e. about 3-5 hours in times of storm. Storm tanks provided for flows in excess of 3 x D.W.F. (cf. page 72) should have a minimum detention period equivalent to 6 hours of the D.W.F. In America, in Scotland, and on the Continent much shorter detention periods are employed (1-3 hours) and have the advantage of preventing the sewage from becoming stale and malodorous. The long detention periods used in this country can perhaps be justified by the fact that English sewages are stronger and more colloidal and therefore more difficult to settle than American sewages, and when the sewage disposal works handles a large variety of industrial wastes the long detention periods do assist in mixing and balancing the various wastes, thus tending to prevent shock loads from passing on to the biological treatment plant.

The removal of suspended solids by plain sedimentation is generally in the region of 50-80 per cent but the amount removed is dependent upon the strength and character of the sewage as well as on the detention period. There is evidence in the literature [23] that an appreciable amount of biological purification takes place during sedimentation.

Part of the suspended matter in sewage is rather finely divided ('pseudo-colloidal') and very difficult to settle. FISCHER and
Hillman have demonstrated both in laboratory and in plant-scale tests in the U.S.A. that improved sedimentation can be obtained with mechanical flocculation in a "Clariflocculator" provided with rotating paddles which cause the finely divided particles to coalesce into larger flocs with improved settling characteristics. The flocs so produced are somewhat easily broken up if stirred too rapidly and the most efficient peripheral speed of the flocculator was found to be 1.4 ft./sec. In this country, Hurley and Lester at the Wolverhampton Corporation's Coven Heath sewage works have carried out large-scale tests showing that at very little cost mechanical flocculation using a Dorr Clariflocculator (a combined flocculator and settling tank) gives an effluent about 20 per cent better than that obtained by plain sedimentation. Mechanical flocculation is considerably cheaper and easier to carry out than chemical flocculation.

Chemical flocculation or precipitation

Neither plain sedimentation nor mechanical flocculation of raw sewage results in the removal of any appreciable portion of the colloidal matter present. Addition of certain chemicals to sewage, however, causes the formation of an insoluble flocculent precipitate which absorbs and carries down suspended matter and colloidal matter and gives a fairly clear supernatant liquor. This process is called chemical flocculation or coagulation. The chemicals mostly used in this way in sewage treatment are lime, aluminium sulphate ('alum' or 'alumino-ferric') with or without lime, copperas in conjunction with lime, and various ferric salts in conjunction with lime. Sulphuric acid is also used to precipitate fatty acids from sewage containing wool scouring wastes (cf. page 422).

The chemical reactions taking place during chemical treatment of sewage are as follows:

**Lime**

\[ \text{Ca(OH)}_2 + \text{H}_2\text{CO}_3 = \text{CaCO}_3 + 2\text{H}_2\text{O} \]

insoluble

\[ \text{Ca(OH)}_2 + \text{Ca(HCO}_3)_2 = 2\text{CaCO}_3 + 2\text{H}_2\text{O} \]

insoluble

It is generally accepted that the lime reacts with all the free carbon dioxide and the carbon dioxide combined as calcium bicarbonate in the sewage to produce an insoluble precipitate of calcium carbonate which acts as the flocculating agent carrying down much of the impurity. A large excess of lime is bad since it dissolves or disperses some of the organic suspended matter and so gives an inferior effluent. This explanation of the action of lime on sewage is rejected by Stones who found that sewage freed from
carbon dioxide and bicarbonate could still be precipitated by lime. Also the effect of lime on sewage was quite different from that of calcium chloride or caustic soda, but a mixture of calcium chloride and caustic soda behaved like lime in coagulating sewage. The experiments of Stones suggest that in the coagulation of the negatively charged sewage colloids lime behaves as if it were a positively charged calcium hydroxide sol. He also showed that to get any appreciable purification of sewage, with a detention period of 18 hours, a lime dosage greater than 250 p.p.m. is necessary but the resulting alkaline liquor must then be neutralized before biological treatment.

Aluminium sulphate

In England, this substance is generally used in a commercial form known as 'alumino-ferric', which consists mainly of hydrated aluminium sulphate containing a small amount of ferric sulphate. In the U.S.A., aluminium sulphate is usually called 'alum'.

Aluminium sulphate reacts with calcium bicarbonate in sewage to give an insoluble precipitate of aluminium hydroxide, which is the flocculating agent:

$$\text{Al}_2(\text{SO}_4)_3 + 3\text{Ca(}\text{HCO}_3\text{)}_2 = 3\text{CaSO}_4 + 2\text{Al(OH)}_3 + 6\text{CO}_2.$$

When insufficient bicarbonate alkalinity is present in the sewage, it may be necessary to adjust the pH by adding lime. Stones, however, maintains that the addition of lime to an essentially neutral sewage is not only unnecessary but may even be a disadvantage. On the other hand, when the alkalinity of the sewage is high (e.g. in the presence of alkaline soapy wastes) it may be reduced somewhat by the addition of sulphuric acid prior to adding aluminium sulphate, thus resulting in some economy since acid is cheaper than aluminium sulphate; this was done by Arderne and Lockett in the pre-treatment of Manchester sewage during prolonged dry spells with the object of rendering the sewage easier to treat by the activated sludge process.

Control of the pH value is very important. According to Garner, the optimum formation of floc when sewage is coagulated with aluminium sulphate occurs between pH 6.3 and 6.5. Other workers, however, have found that the optimum pH is around 5.9. The amounts of aluminium sulphate required for flocculation are generally in the region of 50-150 p.p.m. so that as a rough guide 4-11 cwt of aluminium sulphate will treat about 100,000 gal. of sewage. To achieve good floc formation, proper mixing and a period of gentle stirring are desirable followed by sedimentation.
Iron compounds

The commonest of these is hydrated ferrous sulphate (known commercially as ‘copperas’) which is used in conjunction with lime. The reactions taking place can be represented by the following equations:

\[
\begin{align*}
\text{FeSO}_{4}\cdot7\text{H}_2\text{O} + \text{Ca(}\text{HCO}_3\text{)}_2 & = \text{Fe(}\text{HCO}_3\text{)}_2 + \text{CaSO}_4 + 7\text{H}_2\text{O} \\
\text{Fe(}\text{HCO}_3\text{)}_2 + 2\text{Ca(}\text{OH}\text{)}_2 & = \text{Fe(OH)}_2 + 2\text{CaCO}_3 + 2\text{H}_2\text{O} \\
4\text{Fe(OH)}_2 + 2\text{O}_2 + 2\text{H}_2\text{O} & = 4\text{Fe(OH)}_3
\end{align*}
\]

Ferric hydroxide (insoluble)

Ferrous bicarbonate is first formed and is converted by addition of lime to ferrous hydroxide and finally to insoluble ferric hydroxide by oxygen present in the sewage or introduced by air-blowing. The gelatinous precipitate of ferric hydroxide acts as an excellent flocculating agent. The pH value after lime addition should be above 7.7 and preferably in the region 8.5-9.0 to ensure satisfactory precipitation.

Ferric salts are excellent precipitants but are not available commercially in large quantities in this country. Chlorinated copperas, a mixture of ferric chloride and ferric sulphate obtained by chlorinating ‘copperas’, was formerly used at the Barking sewage plant for the treatment of much of the London sewage before discharge to the River Thames.

The so-called ‘Niers process’ is used in Germany for the treatment of sewage containing a large proportion of textile and tannery wastes.28, 28a. The sewage is treated with iron chips and saturated with carbon dioxide (flue gas), which results in the formation of ferrous bicarbonate:

\[
\text{Fe} + 2\text{CO}_2 + 2\text{H}_2\text{O} = \text{Fe(}\text{HCO}_3\text{)}_2 + \text{H}_2
\]

Aeration then converts the ferrous bicarbonate to flocs of ferric hydroxide which assists in precipitating polluting matter:

\[
4\text{Fe(}\text{HCO}_3\text{)}_2 + 2\text{H}_2\text{O} + \text{O}_2 = 4\text{Fe(OH)}_3 + 8\text{CO}_2
\]

Chemical precipitation does not find extensive use in this country today in sewage treatment though it is an important method for the treatment of trade wastes (see page 509). But it is sometimes useful for the preliminary treatment of sewage prior to biological filtration in cases where the sewage contains a large proportion of trade wastes, where a plant is overloaded, or where seasonal variations occur in the volume and strength of the sewage (e.g. at coastal resorts). Owing to the precipitation of large amounts of inorganic solids, chemical precipitation produces much more sludge than does plain sedimentation.
The purification obtained by chemical precipitation is intermediate between that given by plain sedimentation and that produced by biological processes. In general, the effluents from chemical precipitation processes are unsuitable for discharge to the comparatively small inland streams in this country. The Royal Commission on Sewage Disposal\(^\text{18}\) did, however, conclude that chemical precipitation of sewage should be sufficient treatment in cases where the dilution by stream water was within the range 150–300 volumes.

**Septic tanks**

Septic tanks are, in effect, sedimentation tanks in which the sludge settling on the bottom is allowed to digest and liquify by anaerobic bacterial action. This conversion of the solids to liquids and gases is, however, only partially accomplished and the sludge has, therefore, to be removed from time to time, though a small proportion is always left in the tank for seeding purposes. A septic tank differs from an ordinary sedimentation tank mainly in the length of retention of the deposited sludge.

The original septic tank of Cameron, constructed at Exeter in 1895, was covered but the Royal Commission on Sewage Disposal decided that this was unnecessary since in practice a thick scum forms on the surface of the tank thus effectively preventing access of oxygen from the air and allowing anaerobic action to proceed. Nevertheless, the Ministry of Housing and Local Government in a recent memorandum\(^\text{31}\) recommends that to prevent accidents all the smaller septic tanks should be provided with covers efficiently ventilated to permit escape of gases, whilst the larger tanks need not be covered but should be surrounded with railings.

Septic tanks have the advantage of needing little attention other than the occasional removal of digested sludge from the bottom (e.g. when more than a quarter of the tank is occupied by sludge and scum, which usually means at 6-monthly intervals) and are therefore favoured for very small communities, such as a few houses. According to ESCRITTI\(^\text{1}\) the amount of digested sludge produced is usually about \(\frac{\text{1}}{4}\) gal. per head of population per day.

The effluent produced, which generally has an objectionable smell, should not be discharged to a stream without further treatment either on land or on a percolating filter\(^\text{31}\). At times, especially in warm weather, the effluent may be even worse than the incoming sewage and may contain more suspended matter due to the buoying up of sludge particles by the evolved gases. This disadvantage can be overcome by using an Imhoff tank\(^\text{3}\) which is really a two-compartment tank in which sedimentation of the sewage and digestion of the sludge are carried out in separate compartments. A few tanks
of this kind are still in use today in this country, Germany (where
they originated) and America.

Although septic tanks are no longer favoured for large sewage
works, they are still largely used in rural areas for individual houses,
or even a few houses, but their use for larger groups of property is
strongly to be deprecated in view of the pollution likely to be caused
by the discharges to the stream.

Contact Beds
A contact bed consists of a large water-tight tank (usually con­
structed of concrete) and containing a suitable graded filtering
medium (e.g. clinker) used for the treatment of sewage by the fill­
and-draw method. Settled sewage is allowed to flow into the bed
where it generally remains for about 2 hours, after which the bed is
permitted to rest whilst the effluent, if insufficiently purified, may
be allowed to pass on to a second bed. The purification taking
place is due to the biological activities of bacteria and other low
forms of plant and animal life in the film which forms on the surface
of the filtering medium some weeks after the bed is first brought into
use. Thus, new beds have first to ‘mature’ (i.e. develop a satis­
factory biological film) before any appreciable purification of
sewage takes place. The contact bed has now been almost com­
pletely replaced in this country and the U.S.A. by the modern
percolating filter or by the activated sludge process, which can deal
with much larger volumes of sewage and can produce much better
effluents.

MODERN BIOLOGICAL METHODS OF SEWAGE TREATMENT

Introduction
When the final effluent from a sewage disposal works discharges
to a relatively small inland stream, which is generally the case in
this country, fairly complete treatment of the sewage is required.
The essential stages in a modern plant in the order in which they
are generally carried out are as follows:

(i) Removal of grit in detritus tanks (page 423).
(ii) Screening (page 423).
(iii) Sedimentation in tanks (page 426) with or without mechanical
flocculation (page 427) or chemical flocculation (page 427).
(iv) Biological treatment by one of the approved modern methods
(percolating filters or activated sludge), which in reality are
an artificial intensification and acceleration of the ordinary
aerobic processes of natural purification that go on in rivers
polluted by limited amounts of organic wastes.
(v) Disposal of the sludges produced in stages (iii) and (iv).
It is necessary to remind the reader at this stage that, in the case of sewage from combined sewerage systems (page 58), biological treatment is provided only for flows up to $3 \times D.W.F.$ (cf. Chapter 4). Storm flows between $3 \times D.W.F.$ and $6 \times D.W.F.$ are given partial treatment by settlement in special storm tanks.

In many places, particularly in plants in the U.S.A. but also at a few modern plants in this country (e.g. at Mogden and Colne Valley), screens, especially the finer screens, which have many unpleasant features and need considerable cleaning and attention, have been replaced by comminutors or macerators. These consist essentially of a slotted drum rotating about a vertical axis in a channel through which the sewage is passing; a series of sharp projecting parts or cutters disintegrate and macerate the coarse solid materials to an extent sufficient to permit passage through the slots. At Mogden the screenings from the screens are delivered by rakes to belt conveyors and after maceration the material is returned to the sewage inlet. At the more recent Colne Valley plant the comminutor combines the role of a screen and macerator. The advantages of comminutors are offset to some extent by the fact that they put an extra load on the next stage of treatment, namely settlement in tanks.

The main features of the two most important modern biological methods of purifying settled sewage, namely the percolating filter and the activated sludge process, will now be reviewed.

**Percolating filters**

Percolating filters (called 'trickling filters' in the U.S.A.) consist essentially of circular or rectangular beds of clinker, slag, stone, coke, coal, or other similar medium (usually 1–1\(
\frac{1}{2}\) in. in size at the top of the filter but 4–6 in. at the base) provided with walls of concrete or brick. The medium is intended to serve as the habitat of bacteria, fungi, and other micro- and macro-organisms which play so important a role in the purification of sewage. The material constituting the medium of a percolating filter should be free from dust, be durable and resistant to the action of the sewage, have a high ratio of surface area to weight, be rough enough to encourage the formation of a biological film, be uniform in size with length, breadth and height very nearly the same, and finally should have a high percentage of voids to permit passage of air. The necessary specifications for filter media are given in a British Standard, and data on the comparative values of different filter bed materials are given by Ball and Goldthorp.

Percolating filters are generally about 6 ft. in depth but may vary from 4 ft. to as much as 10 ft. A suitable underdrainage system must be provided to carry away the purified sewage and the process,
being aerobic, requires adequate ventilation of the beds. The settled sewage is sprinkled over the circular or rectangular beds by means of rotating or travelling distributors or sprinklers; the old type of fixed distributor is now obsolete. At first the sewage passes through practically unchanged. Gradually, the medium in the beds becomes covered with an active gelatinous biological film (containing bacteria, protozoa, fungi, etc.) which, in the presence of sufficient oxygen from the air, breaks down and stabilizes the putrescible organic impurities in the sewage with formation of carbon dioxide, water, nitrates, sulphates, phosphates and dark brown insoluble humus material. Percolating filters are thus properly called 'biological filters' but the term 'filter' is really a misnomer since the purification achieved is not due to a physical process of straining out the impurities but is largely brought about by biological agencies.

Goldthorpe has given the following very poetic description of the changes taking place when sewage is sprinkled over a percolating filter:

'... the liquid spreads out in a thin film over the surface of the material exposed to the air, in the voids of the material. Hundreds of small rivulets trickle through reed beds of fungal hyphae, join in minute pools and redisperse to seep through morasses of active slime. Countless forms of plant and animal life swarm in the forests, rivers, pools, and swamps of this world in miniature. The plant-like growths secrete sticky juices to attract and liquefy solid matter, and by taking in soluble salts increase their growth. Animals ingest solids and plant growths, and also prey on one another. Polluting substances, whether soluble or not, are arrested, absorbed and changed until, in the case of a normal bed, they emerge with the effluent in which the demand for oxygen is so reduced that when the liquid portion is discharged to a river it is stable enough not to lower dangerously the dissolved oxygen content of the river on its journey to the sea.'

As in the analogous case of contact beds, an adequate period of time is required for the maturing of the filter beds (i.e. the establishment of a well-balanced biological film) before efficient purification of the sewage can occur, and this may be only a few weeks at summer temperatures, when growth of organisms is rapid, but may take several months in the winter. It is therefore preferable, if circumstances permit, to start up a new filter during the warmer months of the year (in this country, May to September).

Percolating filters are in reality a development on an intensified scale of the older method of land treatment. Whilst, however, the amount of settled sewage that can be treated on land even under the

...
best conditions rarely exceeds 5 gal. per cubic yard of land per day, a well-designed percolating filter can be dosed with an average strength domestic sewage at about 14 times this rate, i.e. at about 70 gal./yd.\(^3\) of filter medium per day. The dosage on a filter depends, of course, on the nature and strength of the sewage and the types of trade wastes present. Thus, at the Bradford, Yorkshire, sewage works\(^8\), where the sewage is very strong and contains a high proportion of wool scouring wastes, the average dry weather loading on the filters is as low as 35 gal./yd.\(^3\)/day. On the other hand, a very weak domestic sewage can be dosed at as high a rate as 100 gal./yd.\(^3\)/day (cf. Table 12 in Appendix). In America, where the sewages are generally weaker than in England and where a high quality effluent is usually not so necessary, rates about double these are commonly used.

The final effluent from percolating filters contains much suspended dark brown solid material ("humus sludge") washed off the filter medium and so, before discharge to a stream, requires efficient settlement in special tanks generally known as "humus tanks". The requirements of the Ministry specify that the capacity of these tanks should be at least 4 hours at D.W.F. (i.e. 14 hours at peak flows of 3 x D.W.F.). Humus tanks require frequent cleaning to remove the accumulation of sludge and the neglect of this precaution is a common cause of unsatisfactory effluents with a high content of suspended matter. Difficulties are sometimes experienced by the rising of sludge to the surface of humus tanks, resulting also in much suspended matter passing away with the humus tank effluent. It is generally agreed that the rising of sludge is caused by an accumulation of nitrogen bubbles produced by denitrifying bacteria which reduce nitrates first to nitrites and finally to nitrogen; this process only occurs when all the dissolved oxygen is used up and therefore is less likely to take place with well-oxidized sludges. MOUNTFORT\(^16\) overcame the difficulty by continuous removal of the humus sludge.

Percolating filters contain large numbers of worms, larvae of flies, spiders, and other animals that feed on the biological film, especially in spring, summer and autumn\(^37-39\). These are the so-called scouring organisms which are of great importance because they are useful scavengers tending to prevent the filter from becoming clogged by an excessive accumulation of biological film on the media\(^40\). During the winter when the activities of these scouring organisms at the surface of the bed are practically non-existent as they retreat deeper into the bed, there is a tendency for the filter to become choked by film. This unpleasant phenomenon is termed "ponding" and, of course, it prevents passage of sewage through the bed. Ponding is often caused by overloading the filter.
for instance by the application of an excessive amount of sewage or of too strong an influent, or a sewage containing too high a content of suspended matter. When the warmer weather returns in spring and early summer, the scouring organisms return to the surface, feed on the surface growths and so relieve the ponding. At this time, excessive amounts of suspended matter pass out with the effluent due to solids becoming loosened, and the filter is said to be 'sloughing' or 'unloading'. Several remedies have been suggested for overcoming ponding, for instance flushing the surface of the filter with water or plant effluent, or chlorinating the effluent. An ingenious method of relieving ponding, described by Bell, involves inoculation of the filters with the water springtail (Achorutes vulgaris), a small purplish-black insect about 2 mm in length, which often appears on filters naturally and feeds upon the fungi clogging the filter as well as on the larvae of Psychoda flies ('moth flies').

A certain amount of smell is naturally associated with the spraying of sewage on percolating filters, the extent of the nuisance being dependent upon the nature of the sewage, the presence of certain trade wastes (dairy wastes, brewery wastes and tannery and fell-mongering wastes being specially liable to produce unpleasant odours), the temperature, and atmospheric conditions. Filters should, therefore, be located at some distance from dwelling-houses. Another nuisance associated with the operation of percolating filters is the presence of large numbers of small flies or midges, the common ones being Psychoda alternata, Psychoda serreni and Anisopus Jerezus. These are particularly objectionable to people living near the sewage works. Many remedies have been suggested for combating the fly nuisance, such as flooding the filter once a week for 24 hours, or the use of chlorine and other chemicals, but none of these procedures is entirely satisfactory. Modern opinion favours the use of intermittent dosage with the newer synthetic insecticides, especially DDT and Gammexane (cf. page 84), which kill the adult flies and control the growth of larvae without affecting either the bacterial population or the efficiency of purification of the sewage. In view of the extremely toxic character of these insecticides to fish, care is needed in their application especially if the final effluents discharge to a fishing stream. Tomlinson and his co-workers, however, state that the samples of effluent obtained from various sewage works using insecticides for fly control generally contained such a small amount of insecticide (as determined by bio-assay) that there should be little danger to fish in a river.

Percolating filters are more than twice as efficient as the older contact beds with the same cubic capacity. As far as large cities are concerned where suitable tracts of land are generally scarce, percolating filters have the disadvantage of occupying very large
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areas. Nevertheless, several important cities have adopted the process, four of the largest installations in the world being Bradford, Yorkshire (53½ acres), Birmingham, Warwickshire (43 acres), Leeds, Yorkshire (42 acres) and Baltimore, Maryland, U.S.A. (30 acres).

The percolating filter is still the most popular and widely used biological sewage treatment process in this country, and, in recent years, much work has been done in America and here to improve the process still further especially when dealing with strong and difficult sewages. High-rate filtration at anything up to about 30 times the normal standard rate (e.g. at rates of 200–2,000 gal./yd.³/day), or even higher, with recirculation of effluent (i.e. dilution of the incoming sewage with returned filtered effluent) has met with much success in many cases 48–51.

If the rate of filtration is not too high (say 200–300 gal./yd.³/day) effluents with a satisfactory B.O.D. are obtained but they are comparatively low in nitrate content. With the much higher rates of filtration adopted in the U.S.A., the effluent will certainly not satisfy Royal Commission standards of purity as the removal of B.O.D. will be 50 per cent or less, but the process may be satisfactory as a partial treatment where there is ample dilution by river water (e.g. in a very large river, or in an estuary).

A high-rate process finding much favour in this country is so-called 'alternating double filtration'. This depends upon the interesting observation first made by Whitehead and O'Shaughnessy, of the Birmingham Tame and Rea District Drainage Board, that a clogged percolating filter could be restored to a healthy condition by dosing it with partially purified sewage effluent from another filter, a procedure which has the effect of disintegrating and removing the biological film causing the ponding. It has been shown by Tomlinson 52 that since in alternating double filtration the biological film alternately forms and disintegrates, the net amount of film is less than in an ordinary single filter and consequently the rate at which the sewage can be treated is much higher.

In practice, the process of alternating double filtration is applied by arranging two filters in series, and when the primary filter shows signs of ponding the order is reversed, the primary filter becomes the secondary filter and the secondary filter becomes the primary filter. The process was first successfully developed by the Water Pollution Research Laboratory for treating dairy waste waters, which had not hitherto responded well to single filtration because of the severe ponding of the filter. The results of the application of the method to Birmingham sewage were described in an outstanding paper by Wishart and Wilkinson 53 who showed that at least twice the usual volume of settled sewage could be efficiently treated, thus enabling
the capacity of a plant to be approximately doubled by the new system. An extra humus tank is required to settle the effluent from the primary filter and it is necessary to provide additional pumping facilities, but the cost of doing this is comparatively small and is more than offset by the saving in the cost of filters. The process might, therefore, well be used to relieve an overloaded percolating filter system. Experiments at Minworth, Birmingham, over a period of 12 years have shown that alternating double filtration is more satisfactory for Birmingham sewage than is high-rate filtration with recirculation and, consequently it has been decided to convert in definite stages the present single filters at Minworth to alternating double filters in order to increase the capacity of the plant. The process might, therefore, well be used to relieve an overloaded percolating filter system. Experiments at Minworth, Birmingham, over a period of 12 years have shown that alternating double filtration is more satisfactory for Birmingham sewage than is high-rate filtration with recirculation and, consequently it has been decided to convert in definite stages the present single filters at Minworth to alternating double filters in order to increase the capacity of the plant. The design allows for the treatment of sewage flows up to \( \frac{1}{4} \) times the D.W.F. by alternating double filtration; the dosage will be 160 gal./yd.\(^3\)/day on the average D.W.F., i.e. 240 gal./yd.\(^3\)/day with flows of \( \frac{1}{4} \) x D.W.F. It is anticipated that for rates of flow between \( \frac{1}{4} \) and 3 times the D.W.F. ordinary single filtration will prove quite satisfactory. It was found that, to obtain satisfactory results with this particular sewage, the effluent from a primary filter should, before application to a secondary filter, have a B.O.D. of less than 40 p.p.m., thus starving the fibrous growths and assisting in their disintegration. MILLS and his associates have found that a strong and greasy military camp sewage containing laundry wastes, which gave an unsatisfactory effluent when treated by single filtration at about 45 gal./yd.\(^3\)/day, yielded an effluent of satisfactory quality when converted to operation by alternating double filtration at an average rate of 71 gal./yd.\(^3\)/day. Experiments were carried out by OLDROYD at the Mitchell Laithes (Dewsbury) sewage works on the high-rate filtration of sewage containing 40 per cent of textile trade wastes (derived from woollen piece scouring and dyeing). It was concluded from the results that with a treatment rate of 200 gal./yd.\(^3\)/day at D.W.F., effluents satisfying river board standards could be obtained either by recirculation or by alternating double filtration (with daily alternations), the latter process generally giving slightly superior results.

One other modification of the percolating filter, which has the advantages of being free from fly and odour nuisance, merits brief mention, namely the enclosed aerated filter. This is an enclosed percolating filter, 12–18 ft. deep, provided with an air-tight cover, ventilated by introducing a current of air downwards through the bed. Several successful installations have been built in Germany and in South Africa. DEKEMA and MURRAY working in South Africa at the Rondebult sewage works, Germiston, found that over a period of 3 years an enclosed aerated filter was able to treat about 2.5 times as much sewage per cubic yard of filter media per day to
the same degree of purity as can an open 6 ft. filter. By using two enclosed filters in series and reversing the order of the filters in a controlled manner, the purification capacity was increased to 3.2 times that of an ordinary open filter. Hunter and Cockburn in a 4-year investigation on the treatment of sewage at the Glasgow (Dalmarnock) sewage works, Scotland, in an enclosed aerated filter and an ordinary open filter found that the enclosed filter treated about twice the volume of sewage per cubic yard per day as the open filter when both filters were giving effluents of similar quality. The increased efficiency of the enclosed aerated filter is probably due in part to the more favourable temperature conditions inside the filter and to the higher rate of aeration but it may also owe some success to the fact that scouring organisms operate at the surface of the filter for most of the year.

These various newer forms of high-rate treatment are proving very useful as means for improving existing overloaded filter plants as in many instances the cost of conversion is not high and often merely involves additional pumping equipment and pipe lines.

A flow diagram showing the standard low-rate percolating filter system of sewage purification is given in Figure 31.

Activated sludge process

This process, which is actually younger than the aeroplane, had its origin in the classical experiments on the aeration of Manchester sewage carried out by Arderne and Lockett, its discoverers, in 1913-14 just before World War I. They published three important papers on the subject with, what must have seemed in those days, the very intriguing title 'The oxidation of sewage without the aid of filters' Previous investigators had tried aeration but had found that the periods of aeration required to bring about oxidation of sewage were so long that it was unlikely that the process would be economically feasible on a large scale, but in these early experiments the mistake was made of rejecting the insoluble deposits of 'humus' which formed. Arderen and Lockett, however, found that by continuing aeration of sewage for about 5 weeks in the laboratory, complete oxidation and nitrification of the sewage occurred but after removal of the oxidized sewage, the deposited solids ('humus') were used to assist in the oxidation of a further quantity of sewage by aeration. This was repeated a number of times, always retaining the accumulated deposits of sludge, when it was found that purification was occurring with progressively shorter periods of aeration as the activity of the sludge increased more and more. Finally it was possible to produce by aeration for only a few hours an effluent at least equal to that produced by percolating filters. It took at least 6 months in the original experiments to produce an adequate.
supply of sludge, which was named ‘activated sludge’, but the time was later much reduced (e.g. by using humus sludge from percolating filters as inoculum) and it is now possible to build up a supply of sludge in a few weeks by aeration of sewage with return of the settled sludge. Ardern and Lockett investigated the air requirements of the process and also carried out experiments to determine the optimum proportions of activated sludge to sewage. The process was evidently biological since sterilized activated sludge was unable to bring about any purification of sewage. The purification of sewage by aeration with activated sludge is now generally regarded as following a similar course to that occurring in percolating filters, i.e. through the agency of bacteria and other microorganisms which bring about the following changes in the order indicated:

(i) coagulation and flocculation of colloids and pseudo-colloids (clarification stage),
ASPECTS OF RIVER POLLUTION

(ii) oxidation of carbonaceous matter (oxidation stage), and
(iii) oxidation of ammoniacal nitrogen to nitrate (nitrification).

The first two stages (clarification and oxidation) take place quite easily, but the nitrification stage is more difficult to carry out with activated sludge than with percolating filters especially when treating strong industrial sewages.

The work of Ardern and Lockett led to the development of the activated sludge process on a large scale so that it has now taken its place alongside the percolating filter as one of the two outstanding modern aerobic biological sewage treatment processes. The activated sludge process has a considerable attraction for large cities where land is scarce since the plant occupies only a fraction of the area of a percolating filter installation. There are now large activated sludge plants operating in many countries, the largest in the world being the gigantic South-West plant at Chicago which will eventually provide activated sludge treatment for 900 million U.S. gallons of sewage per day. The largest in this country is at Mogden, Middlesex, near London 33, 62, which deals with a D.W.F. of about 70 million imperial gallons of sewage per day from a population of about 1,400,000. Other large activated sludge plants are at Colne Valley (Rickmansworth), Sheffield, and Manchester (Davyhulme). A number of very effective small and medium-size plants of modern design have been constructed in recent years in Lanarkshire, Scotland, and they resemble many American plants in their pleasing design and lay-out with ornamental flower-beds, shrubs and trees 66–68.

Ardern and Lockett in their original investigations laid great stress on the importance of ensuring intimate contact between activated sludge and sewage during aeration. Several methods can be adopted on a large scale for introducing oxygen from the air and mixing the sludge and sewage so as to keep the sludge in suspension, the most important being the following:

(i) Diffused air system 62, 69
This involves the use of compressed air which by the aid of porous tiles or porous domes is bubbled through sewage in aeration tanks about 15 ft. deep. The detention period in the tanks is generally about 6–12 hours at D.W.F. This system, a proprietary method of Messrs Activated Sludge Ltd., London, is used at Mogden 32, Colne Valley 33 and in one of the activated sludge plants at Manchester (Davyhulme).

(ii) Mechanical aeration systems
(a) Simplex surface aeration system 62—In these plants, made by Messrs
Ames Crosta Mills and Co., Ltd., Heywood, Lancashire, an inverted rotating cone with steel blades draws the sewage up a steel tube in a tank and sprays it on to the liquid surface in the aeration tank thus causing intense aeration. The latest type of aerator, embodying high intensity cones, differs from the old type in proportions and in the form and disposition of the blades; it treats at least 50 per cent more sewage than the older type and is being used with success at Burnley, Halifax, Bury and Bolton.

(b) Kessener brush system—This system, first introduced about 25 years ago by Dr Kessener, of Holland, bears some resemblance to the Simplex system. Aeration and agitation is carried out by means of brushes of stainless steel revolving partly submerged in the mixture of activated sludge and sewage. There are at present two plants of this type in England, at Rochdale and Stockport.

(c) Sheffield bio-aeration system—This system, used for example at Sheffield, Stockport and Stalybridge, consists of a series of very long shallow channels, about 4 ft. deep, in which aeration is brought about by vertical revolving paddle wheels which keep the sludge in suspension and set up a wave motion inducing aeration. The efficiency of this process has been greatly improved by EDMONSON by the use of triangular paddle blades instead of the old rectangular ones and by increasing the speed of rotation from 15 rev/min to 30 rev/min. In this way, at least 60 per cent more sewage can be treated.

A flow diagram of the activated sludge process is shown in Figure 32. An important feature of the process is that like biological filtration it is continuous. After the mixture of sewage and sludge has been treated by aeration and settled, part of the sludge is returned to the inlet of the aeration tanks so as to give a mixture of sewage and sludge in the aeration tanks containing about 1,000–3,000 p.p.m. of suspended solids.* or about 10–20 per cent by volume as measured after settlement for 1 hour in a litre graduated cylinder. The optimum proportion of sludge to sewage depends upon many factors, such as the kind of plant, the tank capacity, the character of the sewage and the amount and nature of the trade wastes present, the degree of purification required, the air supply, etc., and must be determined experimentally in each case. An approximate estimation of the amount of activated sludge to be returned to the aeration units can be obtained by using the following formula suggested by LAMB:

* In this country, the figure is generally in the region of 2,000 p.p.m.
where \( g \) = flow of return sludge in gallons per day

\( G \) = flow into aeration tanks in gallons per day

\( p \) = percentage of sludge by volume in aeration tanks (after 1 hour’s settlement in cylinder)

\( P \) = percentage of sludge by volume in return sludge (after 1 hour’s settlement in cylinder)

Another method of calculating the amount of return sludge based on the use of the sludge index test is given by Bloodgood. The sludge returned to the aeration tanks is generally re-activated by
AERATION in order to maintain its activity at a high level, this being specially desirable if a strong sewage is being treated.

In order to secure economy of air or better utilization of air at some activated sludge plants in the U.S.A., modified forms of aeration have been used and these are claimed to give better and more flexible control and reduce costs of operation. Since the rate of oxygen utilization by activated sludge-sewage mixtures is greater during the first two hours than later on, some operators have applied air at a higher rate in the earlier stages (e.g. the first half of the aeration tanks), a modification called 'tapered aeration'.

When the usual method of adding return activated sludge to the whole of the sedimentation tank effluent gives poor results, a modification known as 'step aeration' has been used by Gould, involving addition of return sludge at two or three points along the aeration tanks.

An important characteristic of activated sludge is its 'quality' or 'condition' upon which its ability to purify sewage efficiently depends. Good quality activated sludge is usually golden-brown in colour and has a pleasant earthy odour provided it is kept well-aerated. If deprived of air for any length of time, however, it darkens and eventually becomes black, septic and evil-smelling. With sewage plants on the combined system, the quality of the activated sludge usually improves after a spell of wet weather, especially in the winter, and deteriorates during a long dry spell, particularly in the summer. The favourable results obtained after wet weather may be due to dilution of the sewage by well-oxygenated rain water as well as to the beneficial influence of soil protozoa washed in by the rain. The condition of a sludge can be diagnosed on the basis of a number of laboratory tests, of which the most important are the following:

(a) the volatile matter content of the sludge,
(b) the determination of sludge activity by measurement of the rate of oxygen utilization (e.g. the 'Nordell number'),
(c) the determination of the filtration rate of the sludge conditioned with ferric chloride,
(d) microscopic examination,
(e) determination of sludge index, and
(f) settleability of sludge.

The most popular of these tests merit further consideration.

Microscopic examination

ARDERN and LOCKETT showed that the microscopic examination of

* The 'Nordell number' is the amount of oxygen in p.p.m. utilized per hour by the sludge and can be determined in an apparatus termed an 'Oxymer'.
activated sludge gave very valuable indications of the quality of the sludge. Satisfactory and good sludges were found to have a preponderance of ciliate protozoa, which move and feed with the aid of cilia or fine hair-like processes. Ciliate protozoa found in good activated sludge include *Carcelemum, Vorticella, Epistylis, Leoplophryum, Choenia, Childon, Colpoda, Colpidium* and *Aspidisca*. Very few flagellate protozoa and very few amoebae and other rhizopods are present in good sludges. Filamentous growths should be absent or present in only small amounts. Rotifers are often present. Unsatisfactory and bad sludges contain a preponderance of flagellate protozoa, which have one or more flagella or fine whip-like processes, but very few ciliates are present. These observations of Ardern and Lockett have been confirmed by later workers, and the presence of ciliate protozoa (especially the peritrichs such as *Vorticella*) can be taken as an indication of a good sludge. The presence of large amounts of filamentous growths is an infallible sign of a poor or bad sludge. REYNOLDS63, working at Huddersfield, where the activated sludge contained only a limited variety of ciliates owing to the presence of chemical trade wastes in the sewage, found that there was a high degree of inverse correlation between the B.O.D. of the effluent and the abundance of *Vorticella* in the aeration tank liquor, i.e. the better the quality of the effluent, the higher is the *Vorticella* count. There is no doubt that *Vorticella* and other ciliate protozoa do play an important part in the purification of sewage. In fact, PILLAI and SUDRAHMANYAM84, from the results of their experiments with the protozoon *Epistylis*, consider that aerobic purification of sewage is essentially due to the activities of protozoa and that bacteria merely play a secondary part! In this connection, SUGDEN and LLOYD65 have described some fascinating experiments with the ciliate protozoon *Caraculum polypium*. They showed that this and several other ciliates have a powerful clarifying effect on turbid waters containing DDT emulsion, Indian ink, or sewage; inert particles and bacteria are thereby removed by ingestion, consolidation and external flocculation by mucus secretions. The movement of the cilia is an important aid in the conveyance of food to the mouth of a protozoon and it would, therefore, appear that the mass effect of the movement of the cilia of protozoa may play an important role in promoting the gentle but adequate mixing of sewage and sludge that is so vital a factor in the activated sludge process.

**Sludge index**

Among the many sludge indexes proposed for activated sludge plant control, that due to MOHLMAN81 is the most frequently used. It is the volume in millilitres occupied by 1 g of activated sludge after
settling the ‘mixed liquor’ (i.e. the mixture of sludge and sewage from the aeration tank) for 30 minutes in a litre graduated cylinder, and is often called the sludge volume index (S.V.I.):

\[
\text{S.V.I.} = \frac{\text{settled volume of sludge percentage (30 min.)}}{\text{suspended solids percentage}}
\]

This index increases as the sludge shows a tendency towards settling badly or ‘bulking’, and usually varies from about 40 for a good sludge to about 200 or more for a poor sludge. Finch and Ivra\(^8\) have pointed out that consolidation has a marked influence on the percentage of sludge settled in 30 minutes, and settlement-time curves show that consolidation usually begins after about 6 minutes. In order to eliminate the influence of consolidation and so increase the sensitivity of the sludge index test for distinguishing between good and bad quality sludges, they suggest that the settled volume percentage in 6 minutes be used in calculating the sludge volume index—this would of course give rather higher index figures. Donaldson\(^9\) prefers to use the sludge density index (S.D.I.) which is given by the expression:

\[
\text{S.D.I.} = \frac{\text{suspended solids percentage} \times 100}{\text{settled volume of sludge percentage (30 min.)}}
\]

This index varies from about 2.0 for a good sludge to about 0.3 for a poor sludge.

Settling ability of activated sludge
Activated sludge in good condition will settle very rapidly from mixed liquor whilst poor sludge, on the other hand, will settle slowly. Curves showing the rate of settlement of good, fair, and poor sludges are shown in Figure 33.

![Figure 33. Typical settlement curves for activated sludge](image-url)
The settleability of activated sludge is dependent on a large number of factors which have been admirably discussed by RUDULF S and LACY and include temperature, the length of time the sludge has been aerated, the suspended solids concentration, the depth or width of the vessel or container, the angle of inclination of the container, the nature of the trade wastes in the sewage from which the sludge is prepared, and the age and degree of septicity of the sludge. Under certain conditions, the density of the activated sludge particles decreases and the sludge loses its characteristic property of rapid settlement, resulting in large amounts of sludge being carried over with the liquid and contaminating the plant effluent. This troublesome phenomenon is termed 'bulking'.

Microscopic examination of bulking sludge often indicates the presence of characteristic filamentous growths of *Sphaerulina natans* and other thread-like organisms, but this is not always the case. The causes of bulking are rather obscure. Such varied factors as overloading the activated sludge plant, the presence of excessive oil and grease, underaeration, overaeration, high concentration of sludge in the mixed liquor, high organic content of the sludge, short circuiting in the aeration tanks, and growths of filamentous organisms have been held responsible for the trouble. Present-day opinion considers that sudden shock loads (especially of carbonaceous wastes) is one of the main causes of bulking. Fortunately, the condition is rare at well-operated large plants which are not overloaded and is mostly confined to the smaller plants where perhaps there may be considerable fluctuations in organic load and in flow and often not as much technical supervision as is desirable. No one remedy is efficacious in correcting bulking in every case but such measures as increasing the quantity of air and the aeration period, addition of finely divided inert materials (e.g. clay, fuller's earth, red marl, etc.), reducing the amount of suspended solids in the mixed liquor, chlorination at controlled rates, and reducing the organic load on the plant by dilution with plant effluent have been reported as successful in some instances. In extreme cases, the bulking sludge must be disposed of (in lagoons, but not to the river!) and a new sludge must be developed. SMIT has shown that carbohydrates such as glucose and ordinary sugar (especially in amounts greater than 0.5 per cent) cause bulking of sludge accompanied by growths of thread-like organisms, but the latter appear to be a symptom of the trouble rather than the cause since it was shown that inoculation of healthy sludge with filamentous organisms does not induce bulking. HEKELKIAN regards bulking as a kind of disease of activated sludge which develops only under unfavourable conditions (e.g. low oxygen supply in relation to the concentration of organic matter in the sewage). He suggests that such tests as
microscopic examination, determination of dissolved oxygen in the mixed liquor, and determination of sludge index should be carried out daily. Any appearance of filamentous organisms, increases in the sludge volume index, or marked fall in the dissolved oxygen content of the mixed liquor will act as warning signs of the development of an unsatisfactory sludge and of the possible imminence of bulking, and so enable the necessary control measures to be instituted before the bulking becomes unmanageable. In addition, of course, tests of the quality of the effluent produced (especially B.O.D., permanganate value, ammoniacal nitrogen, stability, nitrate content, and suspended solids) should be carried out daily.

Although for reasons of economy nitrification of sewage is not normally carried out at activated sludge plants, at the more modern plants where power is obtained from sludge gas, a high degree of nitrification is achieved (cf. page 376). The advantages of carrying the purification to an advanced stage of nitrification have been reviewed by Townend and Lockett in connection with the Mogden plant and include production of a dense easily settleable sludge, freedom from sludge bulking, large reduction in the volume of surplus activated sludge, greater capacity for dealing with overloads, production of a well-nitrified effluent low in ammoniacal nitrogen and much superior for the preservation of good river conditions, and finally production of a sludge which is more amenable to dewatering. During the past few years, however, nitrification at Mogden has fallen off considerably and is now stated to be 'virtually non-existent'; the cause is probably the rising load on the plant coupled with the greatly increased use of synthetic detergents. Other activated sludge plants (e.g. Manchester) have noted a deterioration in their final effluent since the increase in the use of synthetic detergents and it is probable that this is due to a reduction in the rate at which oxygen is absorbed by the mixed liquor. Indeed, experiments carried out at the Davyhulme sewage works of Manchester Corporation have shown that when deoxygenated water is re-aerated by means of a current of air, less oxygen is absorbed in the presence of a detergent. Thus, 10 p.p.m. of 'Tide' caused a 3 per cent diminution in dissolved oxygen content and 25 p.p.m. of 'Tide' an 18 per cent fall. Many eminent sewage experts are of the opinion that those synthetic detergents which are resistant to oxidation at the sewage works should be prohibited either by force of public opinion or even by means of legislation.

Laboratory experiments carried out by Greensberg, Klein and Kaufman have shown that a deficiency of phosphorus in sewage treated by activated sludge has an adverse effect on the quality and activity of the activated sludge, causing poor settling, growth of undesirable filamentous organisms (e.g. Sphaerotilus natans), and
reduced B.O.D. removals. The minimum concentration of phosphorus required is apparently dependent upon the B.O.D. loading and upon the concentration of suspended solids in the "mixed liquor". In the experiments of these authors, in which the concentration of suspended solids was 1,500 p.p.m. and the B.O.D. loading was 15-8 lb. per day per 1,000 ft.³ of aeration capacity, the phosphorus requirement was about 9-8 p.p.m., corresponding with a B.O.D.:P ratio of 238:1.

**OTHER METHODS OF SEWAGE TREATMENT**

*Fish ponds* 95, 96

As an aid to the natural biological purification of sewage, fish ponds have been in use for many years in Germany and in India. Settled sewage free from toxic materials is admitted to a shallow pond or lake at a number of points. About 1 acre of pond should be provided for every 1,000 of contributing population. The dilution with clean well-oxygenated water should be about 3 volumes of water to 1 volume of settled sewage. The dissolved oxygen content of the pond must be kept fairly high (say 80 per cent of saturation or over) and must not fall below 3 p.p.m. The ponds are stocked in spring with ducks and with fish (e.g., carp, tench, or even trout) which in Germany find a ready sale. The ponds are emptied and cleaned out during the winter but, according to Rohm 95, the provision of two ponds simplifies the cleaning arrangements. At Munich 97, where the ponds occupy 575 acres and require only 1/6 of the area needed for broad irrigation, the detention period is about 2 days, the optimum pH lies between 7-2 and 8-0, and the effluent produced is at least as good as that obtained by land treatment. Falck 98 states that the use of fish ponds provides the most satisfactory method for the purification of sewage in Germany and is more profitable than the best farm land. The sewage used in fish ponds should not be septic, otherwise the fish might acquire an unpleasant flavour 99.

*Oxidation ponds* 100, 101

These are shallow artificial basins or lagoons receiving a continuous flow of settled sewage and having a minimum detention period of about 4 weeks, during which time biological stabilization takes place giving a stable effluent containing some nitrate and having a low B.O.D. According to Oswald and his associates 102 the breakdown of the sewage organic matter by bacterial action to carbon dioxide and ammonia occurs during the first 10 days and causes a fall in dissolved oxygen. This phase is succeeded later by the development of algae, and a rise in dissolved oxygen takes place
owing to photosynthetic activity. These two phases, the bacterial phase and the algal phase, are not necessarily sharply separated but may overlap to some extent. Effluents from oxidation ponds are better bacteriologically than effluents from other biological processes but they may be turbid and greenish owing to the presence of algae (e.g. *Euglena*) in suspension.

Although this method has occasionally given satisfactory results in temperate climates, it has been applied most successfully in semi-tropical areas, such as California, Nevada and Arizona, where level land is cheap and easily available and where favourable climatic conditions exist (e.g. low rainfall, much sunshine, and high air temperatures). The breakdown of organic matter is most rapid during the long warm summer days when maximum photosynthesis occurs.

At Nottingham, England, the work of Stone and Abbott has shown that the photosynthetic activities of algae can play a considerable part in sewage purification.

Oxidation ponds can also be used to follow conventional biological treatment processes in order to yield an improved final effluent. This is done, for example, in this country at Bradford where the humus tank effluent from the Esholt sewage works passes to a large clarification lake (area: 14 acres) before it discharges to the river.

Owing to the presence of living algae, which can exert an oxygen demand when incubated in the standard B.O.D. test, Parker and his co-workers assess the performance of oxidation ponds on the basis of the filtered B.O.D. rather than the B.O.D. of the unfiltered effluent. They have also demonstrated the possibility of treating raw sewage in Australia by passing it through anaerobic lagoons, where anaerobic digestion and partial B.O.D. removal take place, and finally in aerobic lagoons where complete stabilization occurs.

**EFFICIENCY OF VARIOUS SEWAGE TREATMENT PROCESSES**

An approximate idea of the amount of purification which can be expected by the application of various treatment processes to sewage, based on data in the literature, is given in Table 84.

It must be emphasized that the figures shown in this table give only a very rough idea of the amount of purification to be expected. In practice, the efficiency of the purification will depend to some extent on such factors as the strength and character of the sewage (a weak domestic sewage giving different results from a strong industrial sewage), the design of the plant, the skill of the technical
staff in charge, and the nature and extent of the supervision given.

<table>
<thead>
<tr>
<th>Process</th>
<th>Approximate reduction percentage (based on raw sewage)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5-day B.O.D.</td>
</tr>
<tr>
<td>Plain sedimentation</td>
<td>30-40</td>
</tr>
<tr>
<td>Septic tank</td>
<td>25-45</td>
</tr>
<tr>
<td>Chemical precipitation</td>
<td>60-75</td>
</tr>
<tr>
<td>Sedimentation + contact beds</td>
<td>50-75</td>
</tr>
<tr>
<td>Sedimentation + percolating filters (low-rate)</td>
<td>80-90*</td>
</tr>
<tr>
<td>Sedimentation + activated sludge</td>
<td>85-95*</td>
</tr>
<tr>
<td>Sedimentation + intermittent slow sand filters</td>
<td>90-95*</td>
</tr>
</tbody>
</table>

* Even higher reductions are sometimes attained.

The experiments of Allen, Tomlinson and Norton\(^{109}\) have shown that there is no definite correlation between the removal of polluting organic matter from sewage by biological filtration and the extent to which bacteria are reduced in numbers, hence the chemical quality of a sewage effluent is not necessarily a guide to its bacterial quality. It must be borne in mind, too, that the actual bacterial counts in well-purified sewage effluents, though much lower than those in sewage, are still very much higher than those permitted by the Ministry of Health (cf. page 98) in drinking water. Thus, Allen and his associates\(^{109}\) found that the effluent from a single percolating filter showed an average presumptive coliform count of 30,000 per 100 ml. in the winter and 42,500 per 100 ml. in the spring, whereas a satisfactory drinking water should have a count of only 1-3 per 100 ml. When vegetables, such as watercress, are grown in sewage effluents or other waters liable to contain bacteria and other micro-organisms, sterilization of the vegetables should be carried out; it has been shown\(^{110}\) that the best method of sterilization is to soak the vegetables for 10 minutes in 0.25 per cent bleaching powder solution—the use of 2 per cent salt solution or of \(\text{Na}_2\text{MnO}_4\) potassium permanganate proved unsatisfactory.

It will be seen from Table 84 that on the basis of B.O.D. reduction, the removal of organic matter from sewage by percolating filters or by activated sludge is very good. On the other hand, the reduction in the bacterial content of the sewage although in some cases reaching 98 per cent is in reality not so satisfactory since the
actual counts are still by no means low compared with what is desirable in drinking water and, moreover, there are such complications to be considered as subsequent after-growth and multiplication of the residual bacteria, which, though relatively few in numbers, may be potentially dangerous. In order to reduce still further the numbers of bacteria in sewage effluents suspected to contain pathogenic bacteria or in effluents discharging to rivers used for public water supplies, sterilization by means of chlorine may be necessary. Leggatt recommends that chlorination of sewage effluents should be carried out so that the residual content of chlorine after 1 hour is at least 0.5 p.p.m. To achieve this, doses of chlorine of 2–5 p.p.m. or even more may be needed depending on the character of the effluent and the time of contact of the chlorine. Chlorination, however, although widely used for potable waters, has not been adopted to any great extent in this country to disinfect sewage effluents. Seasonal chlorination is carried out at many places in the U.S.A. and elsewhere at seaside resorts or lakes where bathing is widely practised. There are some objections to the general adoption of the practice of chlorinating sewage effluents quite apart from the cost involved and the fact that not much is known about the effect of chlorinated sewage effluents on streams. McLachlan and Gaillard concluded from their experiments in South Africa that complete sterilization of well-oxidized sand filter effluents from several Johannesburg sewage plants required such high dosages of chlorine that chlorination would not prove to be a practical measure. Since chlorine is highly toxic to fish (cf. Chapters 3 and 7) overchlorination of effluents must be avoided otherwise there might be a risk of fish mortality in a stream where the chlorine content is much above about 0.1 p.p.m. Chlorination of effluents from the biological treatment of sewage containing gas liquor has been shown by Allen, Blezard and Wheatland to give liquids very toxic to fish due to the interaction of chlorine with thiocyanates (derived from gas liquor) to produce highly.
Table 86. Results of treatment of sewage at a few representative plants in England

<table>
<thead>
<tr>
<th>Authority</th>
<th>Manchester</th>
<th>Colne Valley</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sewage Works.</td>
<td>Davyhulme</td>
<td>Maple Lodge</td>
</tr>
<tr>
<td>D.W.F. gal./day.</td>
<td>50,000,000</td>
<td>8,000,000</td>
</tr>
<tr>
<td>Average flow gal./day.</td>
<td>63,000,000</td>
<td>8,300,000</td>
</tr>
<tr>
<td>Population</td>
<td>825,000</td>
<td>—</td>
</tr>
<tr>
<td>Trade Wastes. Per cent by vol. of D.W.F.</td>
<td>About 40</td>
<td>20</td>
</tr>
<tr>
<td>Nature of Trade Wastes.</td>
<td>Textile, dye manufacturing, chemicals, paper, metallic waste, soap, etc.</td>
<td>Gas liquor, paper, brewing</td>
</tr>
<tr>
<td>Period.</td>
<td>Year ending 31 March, 1952</td>
<td>June 1952</td>
</tr>
<tr>
<td>Treatment</td>
<td>Activated sludge (diffused air) (Units 3–7)</td>
<td>Activated sludge (diffused air)</td>
</tr>
<tr>
<td>Reference (see end of chapter)</td>
<td>114</td>
<td>33</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Crude sewage</th>
<th>Settled sewage</th>
<th>Final effluent</th>
<th>Crude sewage</th>
<th>Settled sewage</th>
<th>Final effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 hours N/80 permanganate value</td>
<td>110.7, 95.2</td>
<td>29.0</td>
<td>129.4</td>
<td>86.7</td>
<td>15.5</td>
<td></td>
</tr>
<tr>
<td>B.O.D. (5 days, 18°C)</td>
<td>241.7, 210.7</td>
<td>18.9</td>
<td>412.6</td>
<td>236.1</td>
<td>13.1</td>
<td></td>
</tr>
<tr>
<td>Ammoniacal nitrogen</td>
<td>26.8, 27.3</td>
<td>24.3</td>
<td>58.7</td>
<td>69.1</td>
<td>8.3</td>
<td></td>
</tr>
<tr>
<td>Albuminoid nitrogen</td>
<td>8.5, 6.5</td>
<td>2.7</td>
<td>11.7</td>
<td>7.0</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>Nitrite nitrogen</td>
<td>—</td>
<td>trace</td>
<td>—</td>
<td>—</td>
<td>0.2</td>
<td></td>
</tr>
<tr>
<td>Nitrate nitrogen</td>
<td>—</td>
<td>1.2</td>
<td>—</td>
<td>—</td>
<td>36.0</td>
<td></td>
</tr>
<tr>
<td>Suspended solids</td>
<td>186, 85</td>
<td>22</td>
<td>387</td>
<td>87</td>
<td>11.9</td>
<td></td>
</tr>
<tr>
<td>Chloride, as Cl</td>
<td>331, 338</td>
<td>308</td>
<td>147</td>
<td>148</td>
<td>143</td>
<td></td>
</tr>
<tr>
<td>Grease</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td></td>
</tr>
</tbody>
</table>

*This plant treated 13,450,000 gal./day.*

poisonous cyanogen chloride (CNCI). Probably other toxic chlorinated compounds (e.g. chlorinated phenols) are also produced. These observations are of great significance since most sewages from large towns in this country contain some gas liquor and consequently chlorination might involve a risk of fish mortality if the chlorinated effluent were discharged to a fishing stream.

Results of the treatment of sewage at a few representative plants in this country are shown in Table 86.

When comparing analyses of effluents and of raw sewages, it must be remembered that the final effluent may not correspond exactly with the raw sewage on account of the time lag through the plant and fluctuations in the composition of the sewage. In this
Table 86—cont.

<table>
<thead>
<tr>
<th>Location</th>
<th>Description</th>
<th>Final Effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td>West Middlesex</td>
<td>Brewery, food wastes, yeast, plating</td>
<td>11 years, 1936-47</td>
</tr>
<tr>
<td></td>
<td>Activated sludge (diffused air)</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>58,000,000 (1947)</td>
<td>10</td>
</tr>
<tr>
<td>Bradford Esholt</td>
<td>Wool scouring, dyeworks, etc.</td>
<td>Acid precipitation + percolating filters</td>
</tr>
<tr>
<td></td>
<td>18,000,000</td>
<td>12 monthly average</td>
</tr>
<tr>
<td>Dewsbury Mitchell</td>
<td>Textile manufacturing</td>
<td>Year ending 31 March, 1951</td>
</tr>
<tr>
<td>Ladles</td>
<td>Wastes</td>
<td>Percolating filters</td>
</tr>
<tr>
<td></td>
<td>6,500,000</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td></td>
</tr>
</tbody>
</table>

**Crude sewage**

<table>
<thead>
<tr>
<th></th>
<th>Settled sewage</th>
<th>Final effluent</th>
<th>Acid precipitation effluent (&gt; alkali sewage)</th>
<th>Final effluent</th>
<th>Crude sewage</th>
<th>Settled sewage</th>
<th>Final effluent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>79</td>
<td>46</td>
<td>11</td>
<td>228</td>
<td>117</td>
<td>26</td>
<td>125</td>
<td>76</td>
</tr>
<tr>
<td>39</td>
<td>162</td>
<td>8</td>
<td>284</td>
<td>22</td>
<td>250</td>
<td>219</td>
<td>48</td>
</tr>
<tr>
<td>9</td>
<td>46</td>
<td>8</td>
<td>8</td>
<td>36</td>
<td>47</td>
<td>47</td>
<td>17</td>
</tr>
<tr>
<td></td>
<td>2.8</td>
<td>8</td>
<td></td>
<td>6</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>235</td>
<td>69</td>
<td>12</td>
<td>120</td>
<td>112</td>
<td>32</td>
<td>121</td>
<td>121</td>
</tr>
<tr>
<td>103</td>
<td>7</td>
<td>120</td>
<td></td>
<td>112</td>
<td>32</td>
<td>121</td>
<td>121</td>
</tr>
<tr>
<td></td>
<td>99</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*No less than 80% of different trade wastes go to the Manchester sewers.*

In connection, it is of interest to know approximately the time taken for sewage to pass through the various stages of treatment at the sewage works, and this is given in Table 85 due to Key. These times are, of course, only approximate and may vary according to the nature, strength and flow of the sewage, the physical characteristics of the plant and other local circumstances. In the U.S.A., much shorter detention periods are given in primary settling tanks, in activated sludge aeration tanks, and generally in percolating filters; it must be remembered, however, that American sewages are weaker than British sewages and do not require such a high degree of purification owing to the very much larger rivers into which the final effluents discharge.
CHOICE OF SEWAGE TREATMENT PROCESS

Where complete treatment of sewage is required, it is generally necessary to have to make a choice between the activated sludge process and percolating filters. Important factors which may affect the choice of process are cost, local conditions, the nature and strength of the sewage, and the quality of effluent required.

A comparison of these two main biological processes is given in Table 87, and this may be used as a rough guide to enable a choice of process to be made.

It must be remembered, too, that there are various modifications of both processes:

Filters—Single filtration, double filtration, alternating double filtration, high-rate filtration with or without recirculation, enclosed aerated filtration.

Activated sludge—Diffused air, Sheffield bioaeration, Simplex, and Kessener brush.

Thus, a very wide, almost bewildering, choice of sewage treatment processes are now available to the engineer designing a sewage scheme, thus enabling him, financial and other considerations permitting, to construct a plant capable of giving an effluent of almost any desired degree of purity.

Table 87. Comparison of percolating filters and the activated sludge process

<table>
<thead>
<tr>
<th>Factor</th>
<th>Percolating filters</th>
<th>Activated sludge filters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial cost</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Operating costs</td>
<td>Work well in summer</td>
<td></td>
</tr>
<tr>
<td>Influence of weather (combined sewage system)</td>
<td>Little needed</td>
<td>In winter, liable to 'ponding' difficulties and freezing</td>
</tr>
<tr>
<td>Technical control</td>
<td>Suitable for strong and difficult industrial sewages</td>
<td></td>
</tr>
<tr>
<td>Nature of sewage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pumping of sewage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Area of land required</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fly and odour nuisance</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Final effluent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Secondary sludge produced</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic detergents</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* May be lower if all the sludge is digested and power is obtained from sludge digester gas.
In the case of very large cities where land is scarce the activated sludge process will be the obvious choice since it needs only a comparatively small site and is free from fly and odour nuisance. The cost of operating such a plant will not be unduly high if the sludges are digested and the digester gas is used for power, as at Mogden. Where an ample site is available and a strong difficult sewage is being handled, percolating filters may be advisable even for a large city (example, Bradford, Yorkshire, cf. page 434). Unfortunately, coke and good quality furnace clinker (generally regarded as the best materials to use for filter media) are becoming scarce and expensive in this country and the cost of construction of new filters is consequently increasing. A considerable saving in cost of construction as well as in area of land required can be achieved by adopting, instead of single filtration, the new process of alternating double filtration, which is being done at Birmingham (page 437), Liverpool, Bedford, and several other towns in England. Another way of dealing with a strong and difficult industrial sewage is to use a combination of processes. For example, in the proposed new regional scheme for Bolton and district, which will eventually deal with a D.W.F. of 23,000,000 gal. per day, the sewage, which

* A 100 ft. diameter, 6 ft. deep, filter, including the distributors, costs about £7,000-8,000 at the present time (1955).

---

**Table 87—cont.**

<table>
<thead>
<tr>
<th>Activated Sludge</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Advantages</strong></td>
<td><strong>Disadvantages</strong></td>
</tr>
<tr>
<td>Low</td>
<td>High*</td>
</tr>
<tr>
<td>Works well in winter in wet weather</td>
<td>Difficulties in dry summer months</td>
</tr>
<tr>
<td>—</td>
<td>Requires much</td>
</tr>
<tr>
<td>Little or no pumping needed since only a low head is required</td>
<td>Rather sensitive to shocks of strong trade wastes</td>
</tr>
<tr>
<td>Small</td>
<td>—</td>
</tr>
<tr>
<td>None</td>
<td>—</td>
</tr>
<tr>
<td>Suspended solids low</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>Usually not so highly nitrified as a filter effluent</td>
</tr>
<tr>
<td>—</td>
<td>Large in quantity</td>
</tr>
<tr>
<td>—</td>
<td>Much foam, especially on air diffusion plants</td>
</tr>
</tbody>
</table>

† Sewages containing inhibitory trade wastes are difficult to nitrify with activated sludge.
is a strong one containing tannery and other wastes, will receive treatment by the activated sludge (Simplex) process and if necessary will then be given additional treatment on filters which will serve the double purpose of further improving the effluent and achieving a considerable degree of nitrification.

There is a tendency in this country today to ask for an effluent of a much better quality than that required by the Royal Commission on Sewage Disposal, especially in cases where the dilution by river water is low and where the watercourse is used as a source of drinking water. For example, the Severn River Board require effluents to have a B.O.D. not exceeding 10 p.p.m. (i.e. half the Royal Commission standard) and a suspended solids content not more than 15 p.p.m. (i.e. half the Royal Commission standard) where the available dilution in the river is appreciably less than 8-fold. In order to achieve these stricter standards, various methods and 'polishing' devices are available of which the following are the most important:

**Larger capacity plant**

A plant of greater capacity than usual can be constructed. This is being done, for instance, at Crawley New Town, on the head water of a tributary of the River Thames, where a large activated sludge plant is being built to give a final effluent having a B.O.D. not exceeding 10 p.p.m. and a suspended solids content of not more than 10 p.p.m.

**Land treatment**

If land is available, land filtration may prove to be satisfactory as a polishing device for the final effluent from percolating filters or from an activated sludge plant. Indeed, the Severn River Board have suggested surface irrigation over grass plots as a simple and economic method of improving sewage effluents. In industrial areas, however, sufficient suitable land may not be available.

**Mechanical flocculation**

Mechanical flocculation (i.e. gentle stirring by paddles revolving on horizontal shafts) was used in laboratory experiments by Hurley and Lester on the removal of fine suspended matter from percolating filter effluents. The paddle speeds were quite low, viz. 15 rev/min, which is equivalent to a peripheral speed of 0.23 ft./sec. In most cases, satisfactory results were obtained; the removal of suspended solids was about 50-60 per cent, and the final effluents contained about 10-12 p.p.m. of suspended solids. Particularly good results were achieved with filter effluents containing large amounts of suspended matter which did not settle readily when
given plain sedimentation. Since the suspended solids removed had a high content of organic matter, mechanical flocculation also effected a considerable improvement in the quality of the effluent as judged by such tests as B.O.D., 4 hours permanganate value and albuminoid nitrogen. On a large scale, the process would be continuous and would require little attention.

Sand filtration
Sand filters require a smaller area of land than does land filtration and can be of the simple straining variety or, if insufficient area is available, of the pressure type. Evans and Roberts found that at Luton over a period of 1 year, sand filters operating at 200 gal./ft.²/hour reduced the suspended solids content of humus tank effluent from an average of 15·4 p.p.m. to an average of 4·2 p.p.m., equivalent to a removal of 73 per cent. This also had the effect of reducing the B.O.D. from 13·0 p.p.m. to 6·7 p.p.m. The effluent has to be of an unusually high quality at Luton as there is virtually no dilution by river water for part of the year (see pages 551-3).

Sand filters also give excellent removal of bacteria, and, in South Africa, where experiments have shown that poliomyelitis virus is absent from sewage effluent filtered through sand (page 57), the Union now insists on the installation of sand filters on all sewage works.

Micro-strainers
A micro-strainer consists of a drum of woven stainless steel fabric rotating on a horizontal axis. Strainers of this type, with 100,000 orifices to the square-inch of diameter 0·045 mm, have been used at Luton side by side with the sand filters (see above) to produce effluents of low suspended solids content and low B.O.D. It was found that the micro-strainers were not quite so effective for this purpose as sand filters but were somewhat cheaper to run; the reduction in suspended solids content over a period of 1 year was from 15·4 p.p.m. to 5·5 p.p.m., and the reduction in B.O.D. from 13·0 p.p.m. to 8·9 p.p.m. A curious feature of the sand filters was that owing to biological action they removed dissolved oxygen from the effluents and gave a marked reduction in ammoniacal nitrogen. On the other hand, the micro-strainers had no effect upon ammoniacal nitrogen and actually slightly increased the dissolved oxygen. Micro-strainers have the advantage of requiring only very small areas of land and they add only about 5–10 per cent to the cost of treatment.

* This does not seem to be disadvantageous as re-aeration of the river occurs in a short time.
Impounding lakes

It is well-known that the storage of sewage effluents in large shallow artificial lakes results in appreciable further purification due to the action of micro-organisms in the presence of dissolved oxygen. The clarification lake at Bradford affords an interesting example in this country (page 449). Although many examples of such impounding lakes exist in Germany and elsewhere (see this Chapter, page 425), the method requires very large areas of land and would, as a rule, be too expensive for general use in England.

Treatment and disposal of sewage sludge

The treatment of sewage involves the production of large amounts of semi-liquid sludges which have to be disposed of without causing pollution, nuisance, or danger to public health. Although satisfactory methods for the treatment of sewage are available, the disposal of sewage sludge still presents considerable difficulties and may be regarded as a problem which has not yet been completely solved. The obvious solution, namely the return of all sludge to the land, is beset with many pitfalls. The magnitude of the sludge problem will be appreciated when it is pointed out that, according to an estimate in a recent Government publication, the amount of wet sludge (primary, activated and humus) produced in England and Wales at sewage disposal works where sludge is separated is about 16,000,000 tons per annum.

The following are the chief types of sludge produced in the course of sewage treatment:

(a) Sedimentation tank sludge or primary sludge—This is greyish-black, often contains much paper pulp, and has a very offensive odour. According to Escritt, the sludge produced when settlement of sewage takes place in hopper-bottom tanks is \( \frac{1}{4} \) gal. per head of population per day with a moisture content of about 97.5 per cent, whilst with mechanically cleaned tanks 1 gal. of sludge per head per day is produced and the moisture content is then about 95 per cent. Sedimentation tank sludge has a high proportion of fatty and greasy material.

(b) Septic tank sludge is black and has an extremely foul smell. It has a much lower content of moisture (about 90-94 per cent) than sedimentation tank sludge. The very objectionable odour of septic tank sludge is probably due to the fact that the sludge is in contact with putrescent sewage during the digestion process.

(c) Chemical precipitation sludge may be grey, brown or reddish-brown in colour and has an offensive odour. It contains much more
mineral matter than sedimentation tank sludge and has a lower moisture content.

(d) **Humus sludge** is greyish-brown and flocculent with a moisture content around 94-97 per cent. When fresh, the odour is not unpleasant. Like activated sludge, it is rather difficult to dewater.

(e) **Activated sludge** is brownish, flocculent and has a pleasant earthy smell when fresh. If allowed to become septic (e.g. when kept in the absence of oxygen) it acquires a very offensive odour. The moisture content of activated sludge is high (98-99.5 per cent) and very large quantities are produced as surplus sludge which creates a difficult problem in dewatering. Activated sludge has a fairly high nitrogen content (5-7 per cent of N, on a dry basis), contains about 2-4 per cent (dry basis) of phosphoric acid \( (P_2O_5) \) and has a high content of organic matter. The high hopes placed at one time on its value as a fertilizer have not so far been realized on account of the difficulties involved in dewatering the sludge and obtaining a dried product suitable for application to the land.

(f) **Imhoff tank sludge and digestion tank sludge**—These sludges are black and rather viscous, and have a not unpleasant tarry odour. Unlike the other types of sewage sludge, they are non-putrescent if properly digested. The moisture content usually ranges from 88-94 per cent. The content of nitrogen and phosphorus is much less than that of other types of sewage sludge.

A brief outline will now be given of the more important methods available for the dewatering of sewage sludges and for their subsequent disposal. The particular method used must depend upon economics as well as upon local conditions, for instance, availability of land, the presence of water-gathering grounds or of streams used for water supply, the demand for sludge as a fertilizer, proximity to the sea, etc. The desirability of removing as much water as possible so as to reduce the volume of the sludge will be evident from the following formulae which give approximately the change in volume of sludge by removal of water:

\[
\frac{V_1 - V_2}{V_2} = \frac{S_1 - S_2}{S_1} = \frac{100 - M_2}{100 - M_1}
\]

where \( V_1 \) and \( V_2 \) are the sludge volumes; \( S_1 \) and \( S_2 \) are the respective dry solids contents (expressed as percentage by weight); and \( M_1 \) and \( M_2 \) are the respective moisture contents (expressed as percentage by weight). It will be seen that the volume of a sludge varies inversely as the percentage of dry solids; thus, a sludge with
94 per cent of moisture occupies only one third of the volume of a sludge having a moisture content of 98 per cent. At Manchester (Davyhulme) as much water as possible is removed from surplus activated sludge by settlement in a well provided with a picket fence thickener which aids in the separation of water by slowly stirring and combing the sludge.

**Drying beds**

The commonest method of dewatering and drying various types of sewage sludge is to discharge the sludge on to specially constructed drying beds containing suitably graded and underdrained clinker, gravel or sand. A sufficient number of beds should be provided so as to permit adequate time for the operations of filling, drying, and eventual removal of the sludge. The area of drying beds provided is generally woefully inadequate. The area depends, of course, upon the type of sludge and upon the nature and method of treatment of the sewage from which the sludge is derived, but for the best results should be such that for undigested sedimentation tank sludge an area of 1 yd.² is provided for every 2–4 persons of contributing population, and for digested sludge 1 yd.² for every 5–8 persons, depending on local climatic conditions. Unfortunately, the drying process depends upon evaporation as well as on draining, and consequently is adversely affected by weather conditions. Most sewage works managers have great difficulty in dealing with their sludge during prolonged wet weather which is often experienced in the North of England even in the summer, and there may be also difficulties during frosty weather. When drying bed capacity is insufficient, recourse is usually had to drying lagoons at least 10 ft. deep, which, when full, must be left until the sludge is sufficiently dry to remove. In the U.S.A., drying beds covered with glass-like greenhouses are sometimes used in order to obviate difficulties connected with the vagaries of the weather. According to Cleland, covered beds reduce the area required for drying beds by about 50 per cent but they are very costly to construct. Addition of a coagulant, such as aluminium sulphate, has been suggested as a means of facilitating and accelerating the rate at which sludge dries; aluminium chlorohydrate (private communication, Messrs Peter Spence and Co., Widnes) has recently been shown to be particularly efficacious in this respect.

Digested sludges usually dry fairly easily on drying beds but sedimentation tank sludge and humus tank sludge do not dry so readily. Activated sludge is difficult to dewater on drying beds. The liquor discharged through the underdrains of drying beds (so-called ‘sludge drainage’) is chemically and bacteriologically of a grossly polluting character and must not in any circumstances
go to a river but should be returned to the sewage inlet for treatment with the sewage.

Disposal on land\textsuperscript{124, 125}

Where adequate areas of land are available, preferably in districts reasonably far from dwellings so as to avoid complaints of smells, sludge can be disposed of in the wet condition by irrigation over farmland followed by ploughing in after the sludge has partially dried. The method does make use of the valuable fertilizing constituents of the wet sludge and any risks of transmission of disease by pathogenic organisms are virtually ruled out if the sludge is ploughed in. To prevent development of acidity and to maintain satisfactory soil conditions, dressings with lime are necessary. According to \textcite{JENKINS1924} the total area of land required by this method of sludge disposal is about 100 acres per million gallons of daily D.W.F. of sewage, or about 27 yd.\textsuperscript{2} per person.

Another method of disposal of sludge on land, often used in conjunction with drying beds (page 460), is to dump the sludge into natural or artificial depressions in the ground called 'lagoons', where the sludge dries slowly and also undergoes slow digestion\textsuperscript{126}. The dried sludge can be used to fill in low-lying land. Lagooning of sludge may cause very objectionable smells particularly when raw sludges are used.

Sludge can also be disposed of by trenching\textsuperscript{127}, i.e. partly filling a number of trenches with sludge and afterwards covering with soil.

In general, it can be said that land treatment of sludge is suitable only for a comparatively small sewage works but it has been used for larger works where ample land is available.

Disposal at sea\textsuperscript{124, 125}

Many towns and cities situated on or near the sea, or having convenient access to the sea by river, dispose of their liquid sludge by dumping it into the sea in deep water. In cases where the city is situated on a river or watercourse, the sludge is loaded on to special sludge vessels and conveyed to sea. Facilities for the storage of the sludges adjacent to the landing stage must be provided and it is obvious that as much water as possible should be removed from the sludge before it is loaded on to the boat. Examples of cities in this country conveying their sludge in special vessels to sea are London (River Thames), Glasgow (River Clyde), and Salford and Manchester (both on the Manchester Ship Canal). The method has the advantage of being independent of all weather conditions except persistent fogs and gales. Although the method was at one
time considered cheap, this is no longer the case owing to rising
costs of fuel, wages, and construction of new sludge vessels.

Filter pressing

Filter presses consist essentially of a series of cast iron plates with
concave faces, and having filter cloth between them. Filtration of
sludge is carried out by forcing the sludge into the presses with
hydraulic rams or pumps; the pressure applied may reach 60-120
lb./in.². Filter cakes with a moisture content as low as 50-60 per
cent can be obtained by filter pressing. Lime is often added to
assist the filtration. The filtrates are of a highly polluting character
and should be returned to the sewage inlet for treatment. Filter
pressing is used at several towns in this country for dewatering
sludge, notably at Halifax and Bradford, where it forms an
integral part of the process used for extracting wool grease from the
acid precipitated sludge. Activated sludge alone is not amenable
to pressing but the work of Edmondson and Lime suggests the
possibility of dewatering a mixture of sedimentation tank sludge
and activated sludge by filter pressing if lime is added to assist
filtration.

Vacuum filtration

Several types of filter are available for the large scale vacuum
filtration of sewage sludges, a popular one being that made by the
Dorr-Oliver Company. This consists essentially of a hollow
cylindrical drum divided into a number of segments and supported
on a horizontal axis so as to be partly submerged in a trough con­
taining the sludge previously conditioned with a chemical coagulant,
usually a salt of iron or aluminium. The drum is covered with a
suitable filter cloth supported on wire mesh. The filter cloth can
be of cotton, wool, glass, nylon, or monel metal. The West Kent
Main Sewerage Board have found that nylon cloth is much
superior to flannel cloth in durability, each nylon cloth normally
lasting 3,000 hours. As the drum passes through the trough,
vacuum is automatically applied through the action of a multiple
valve and a layer of sludge (usually 1-3 in. thick) is picked up. As
the cake emerges from the trough, vacuum causes air to be sucked
through which aids in the drying of the cake. Before discharge, a
slight air-blow replaces the vacuum thus loosening the cake and
permitting its removal by a scraper. The process is thus a con­
tinuous one but is by no means simple and straightforward, being
influenced by such factors as the kind of coagulant used, the amount
of coagulant, the type of sludge filtered, and the physical and

* Ferric chloride is usually better than chlorinated copperas, and both these
cogulants are superior to aluminium sulphate.
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Chemical characteristics of the sludge. All types of sludge (activated, digested and sedimentation tank sludge) can be dewatered on a vacuum filter. Activated sludge should be as dense and as fresh as possible and is preferably aerated for 2 hours before conditioning with coagulant. Aeration has the effect of reducing the methyl orange alkalinity as well as oxidizing reducing substances and is an important method of securing economy in the use of coagulant. Another method of reducing coagulant consumption, especially in the case of digested sludge, is elutriation. This method, first suggested by Genter, consists of washing the sludge with water or plant effluent to remove ammoniacal compounds, substances which reduce ferric salts to ferrous salts, and finely divided solids interfering with filtration, and then allowing the sludge to settle. The cake from a vacuum filter, which usually has a moisture content of 70-90 per cent, must be further dried, preferably by mechanical methods, when it can be used as a manure or can be incinerated. The output of cake from a vacuum filter depends upon the type of sludge and usually ranges from 2-6 lb. of dry solids per square foot of filter area per hour. Advantages of vacuum filtration are that it is a continuous mechanical process, it occupies very much less space than drying beds, it does not give rise to objectionable odours, it is independent of weather conditions, and yields a product which can be used as a fertilizer. On the other hand, the cost and technical supervision necessary tend to offset these advantages in any but the larger plants. Generally the best coagulant is ferric chloride, which has been popular in the U.S.A. but is no longer available on a large scale in this country. Chlorinated copperas, which can easily be made by chlorinating copperas (ferrous sulphate), is cheaper to use than ferric chloride but the rate of filtration of the coagulated sludge is slower. In this country chlorinated copperas has been used for coagulating mixtures of activated sludge and elutriated digested sludge prior to vacuum filtration at the works of the Colne Valley Sewerage Board. At the St. Helens (Parr) activated sludge plant now under construction, the whole of the sludge produced (primary sludge and surplus activated sludge) will be digested, elutriated with water, coagulated with chlorinated copperas, and finally dewatered on vacuum filters. The use of a rather novel coagulant, aluminium chloride, is reported by Barraclough, who found in pilot plant experiments at Reading that it was superior to either aluminium chloride or to chlorinated copperas as a sludge coagulant, a lower dosage being required and a higher output of cake being obtained on the vacuum filter. Similar results, using aluminium chloro-

* At West Kent, the vacuum filters cover only 100 yd.² whereas the former sludge drying beds occupied an area of 57,000 yd.².
hydrate, have been reported by the West Kent Main Sewerage Board.\(^{134}\)

**Sludge digestion\(^{124}, 137\)**

When sedimentation tank sludge is stored for any length of time, as in a septic tank or Imhoff tank, the sludge undergoes fermentation by anaerobic bacteria that thrive under acid conditions. Bacteria inducing an alkaline fermentation soon, however, replace the acid-forming organisms—especially if a little lime is added—and eventually the sludge undergoes fairly complete digestion with production of gas containing about 70 per cent of methane and about 30 per cent of carbon dioxide. It is usual nowadays to carry out the digestion of sludge as a continuous process in special separate sludge digestion tanks, and, to accelerate the process, which is slow at ordinary temperatures, it is carried out at about 80-90° F ("mesophilic digestion").\(^*\) The heat necessary to raise the sludge temperature is produced by the combustion of the sludge gas which has a high calorific value (about 700–750 B.Th.U./ft.\(^{3}\)). Generally, digestion is complete in about 3–4 weeks, compared with 2 months or more at ordinary temperatures. Still further acceleration of the digestion (to 4–10 days) can be achieved by heating the sludge to about 120–130° F ("thermophilic digestion") but this high temperature is not easy to control and foul odours are apt to be produced as well as a very foul supernatant liquor.\(^{138}, 139\)

Digestion is often carried out in two stages, first in primary tanks for 7–10 days at 80–90° F, and then in secondary tanks at ordinary temperatures to permit further digestion and separation of supernatant liquor. Activated sludge and humus sludge do not give satisfactory results when digested alone but undergo digestion readily when mixed with sedimentation tank sludge.\(^{130}, 138, 140\) Among the advantages of digesting sewage sludges are: (i) reduction in the volume of sludge handled by about two-thirds; (ii) offensive odour of sludge is replaced by a not unpleasant tarry odour; (iii) digested sludges usually dry more easily on drying beds; (iv) digested sludge is safer to use as a manure than undigested sludge which may contain pathogenic organisms; and (v) the surplus gas produced during digestion can be utilized for power purposes in gas engines or in dual-fuel engines, as practised in this country at Mogden\(^{32}\) and Colne Valley\(^{33}\).

The efficiency of digestion tanks can be measured by the extent to which organic matter in the sludge is destroyed, the reduction in organic matter being often 50 per cent or more. The percentage

\(^*\) This is much higher than the calorific value of coal gas (about 480 B.Th.U./ft.\(^{3}\)).
reduction in organic matter can be calculated by the following formula due to Van Kleck [141].

\[
\text{Percentage reduction in dry organic matter by digestion} = \left( \frac{1}{\frac{\text{Percentage ash in raw sludge}}{\text{Percentage organic matter in raw sludge}} \times \frac{\text{Percentage ash in digested sludge}}{\text{Percentage organic matter in digested sludge}}} \right) \times 100
\]

During sludge digestion, especially in the secondary tanks, much supernatant liquor separates; this liquor is of a very polluting character and is often returned to the sewage inlet in controlled amounts for treatment with the sewage.

In the U.S.A., garbage is sometimes disposed of in the sewers. This practice increases the amount of sludge produced and consequently a sludge digestion plant of larger capacity is required. The mixed sewage sludge and garbage solids digest quite easily and give greatly increased yields of gas [142, 143].

Apart from gas production as an indication of favourable digestion, the character of the digested sludge is a good guide as to whether digestion is proceeding satisfactorily or not. Giles [144] has compared the characteristics of well-digested and badly-digested sludges and these are shown with slight modifications in Table 88.

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>Well-digested sludge</th>
<th>Badly-digested sludge</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colour</td>
<td>Black</td>
<td>Brown or grey</td>
</tr>
<tr>
<td>Odour</td>
<td>Tarry</td>
<td>Septic</td>
</tr>
<tr>
<td>Supernatant liquor</td>
<td>Fairly clear</td>
<td>Very turbid</td>
</tr>
<tr>
<td>Gasification</td>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>pH</td>
<td>6.6-7.6</td>
<td>&lt;6.0</td>
</tr>
<tr>
<td>Alkalinity to methyl orange (p.p.m., as ( \text{CaCO}_3 ))</td>
<td>Not less than 2,000</td>
<td>&lt;1,000</td>
</tr>
</tbody>
</table>

Metallic wastes discharged to the sewers generally accumulate in the sludge settling out in sedimentation tanks and in this way toxic concentrations of metals may build up and have an injurious effect upon sludge digestion. Rudger [145] found that a discharge of copper waste producing a sewage containing 0.7 p.p.m. of copper gave a raw sludge with a copper content of as much as 3,700 p.p.m. (on a dry basis). The effect of copper on sludge digestion varied inversely as the concentration of copper in the sludge (dry basis); whilst about 2,500 p.p.m. of copper in the sludge (dry basis) had a negligible effect upon gas production, 13,000 p.p.m. gave only 35 per cent of the normal gas production, and 50,000 p.p.m. only 5 per cent.
per cent of the normal gas production. Other metals which interfere with or retard sludge digestion are nickel\(^{146}\), zinc\(^{147}\), mercury\(^{147}\) and chromium\(^{148}\); the effect is probably due to the toxic influence of these metals upon the anaerobic bacteria bringing about digestion of sludge.

**Heat treatment under pressure**\(^{125}\)

When sewage sludge is heated under a pressure of about 150 lb./in.\(^2\) to a temperature of approximately 360°F for about 45 minutes, its gel structure is completely broken down. This conditioning treatment is so effective that, after cooling, the sludge can easily be densified by simple settlement and then dewatered in filter presses to give a cake of low moisture content. This process has been much improved by the firm of W. K. Porteous Ltd. and is therefore often called the 'Porteous process'. It has been successfully used by Lumb\(^{149}\) at Halifax for dewatering a mixture of humus and activated sludges from which a cake of moisture content about 50 per cent is obtained within 2 days. Among the many advantages of this process are its independence of weather conditions, its freedom from odour nuisance, its applicability to difficult sludges (e.g. humus and activated sludges), the favourable cost compared with other methods, the production of a completely sterile product free from pathogenic organisms and suitable for use as an organic manure, and the small area occupied by the plant (about one-sixteenth of the area required for a digestion plant and drying bed scheme). The liquor produced in the heat treatment process is very foul with a 5-day B.O.D. of about 4,600 p.p.m.; it was dealt with by Lumb without trouble or significant effect on sewage treatment by returning it, balanced over the day, to the influent to the sedimentation tanks, so that it received settlement followed subsequently by either biological filtration, or activated sludge treatment in a Simplex plant. Other plants using the Porteous process have been operated at Horsham\(^{150}\) and Luton\(^{151}\) but have now ceased operation on account of high cost.

**Utilization of sewage sludge as fertilizer**\(^{152-155}\)

Sewage sludge, like farmyard manure, contains substances of considerable fertilizing value, such as nitrogen, phosphorus, potassium, humus, minor essential elements (especially magnesium, manganese and boron), and organic growth-promoting substances\(^{156-158}\). According to a memorandum issued by the Agricultural Research Council\(^{155}\), sewage sludges have a moderate value as sources of slowly available nitrogen and phosphate, but being deficient in potassium content are definitely inferior to farmyard manure for crops needing much potash. Owing to high transport costs only
comparatively dry sludges (i.e. containing less than 50 per cent of moisture) are likely to be generally useful as manures. Dried activated sludge has a higher nitrogen content than any other sludge derived from sewage but unfortunately the wet sludge is more difficult to dewater and dry than are other sewage sludges.

It must be pointed out that a large proportion of the valuable fertilizing material in sewage, especially nitrogen, phosphorus and potassium, does not find its way to the sludge since it is lost in the treated effluent which discharges to the river and eventually to the sea. According to a recent Government report\textsuperscript{159}, about 75 per cent of the nitrogen in sewage is lost in this way (as soluble ammonium compounds and nitrates) in England and Wales, or about 60,000 tons of nitrogen per annum. A possible method of recovering these soluble fertilizing constituents has been indicated by Howard\textsuperscript{160} who suggests, for this purpose, growing the prolific water-hyacinth (Eichhornia crassipes) in sewage effluents. This plant can absorb nitrogen compounds, potassium salts, and phosphates from the effluents and the valuable salts can eventually be recovered by composting the plants to give an organic manure. Experiments at Bradford, however, have shown that these plants do not survive an English winter but the method may prove to be of considerable value in warmer climates\textsuperscript{161}.

Typical analyses of different types of sewage sludge are given in Tables 89 and 90. Although the figures do give some idea of the approximate order of magnitude of the constituents, it must be emphasized that the composition of a sludge depends not only on the type of sludge but also on the nature of the sewage and the quantities and characteristics of the trade wastes in the sewage.

Some care must be exercised in using, as fertilizers, sludges derived from industrial sewages containing metals, as toxic metals may be present in sufficient concentration either to have adverse effects on plant and animal life in the soil or to immobilize the phosphate as insoluble phosphate.

The use of sewage sludges for fertilizing crops is not unattended with risks to public health especially when crude undigested sludges are used in warm climates. Vegetables grown in this way, particularly salad vegetables, should not be eaten raw unless soaked in a suitable sterilizing solution, such as a solution of bleaching powder\textsuperscript{164}. Although the use of properly digested sewage sludge is usually regarded as fairly safe, there is still the danger in tropical and semi-tropical countries of the presence of viable eggs of many intestinal parasites. It has been shown by CRAM\textsuperscript{165} that the eggs of the intestinal round worm Ascaris and of hookworm (which are common in sewage and sewage sludge in tropical climates) can withstand quite long periods of sludge digestion and subsequent
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drying of the sludge but the cysts of Endamoeba histolytica were much less resistant. Ascaris eggs (which are extremely resistant to dry­
ing) were, however, destroyed by heating the powdered sludge containing the eggs to 103°C for 3 minutes. Results obtained by Hogg[166] suggest that an effective method of destroying Ascaris ova in sludge is to dry the sludge in the sun in thin layers (1/2 in.) for long periods. It would appear, therefore, that the use of heat­
dried or sun-dried sewage sludges which have been properly digested should involve little or no danger to public health.

Table 89. Analysis of dried sewage sludges

<table>
<thead>
<tr>
<th>Type of sludge</th>
<th>Slaughter works</th>
<th>Analysis on dry basis: percentage</th>
<th>Reference (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activated</td>
<td>Pasadena</td>
<td>Organic and collate matter 70-75</td>
<td></td>
</tr>
<tr>
<td>Activated</td>
<td>Milwaukee</td>
<td>Nitrogen as N 5-3-6-7</td>
<td></td>
</tr>
<tr>
<td>Activated</td>
<td>New York City</td>
<td>Phosphate as P2O5 7-2-3-7</td>
<td></td>
</tr>
<tr>
<td>Humus</td>
<td>Birmingham</td>
<td>Potash as K2O 0-1-0-5</td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>Honolulu</td>
<td>Matter extracted by Ethyl chloroform 10-12</td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>Indianapolis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary</td>
<td>Baltimore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary + humus</td>
<td>Farnworth</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary + humus</td>
<td>Hacken</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary + acti­vated</td>
<td>Halifax</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary + acti­vated</td>
<td>Grand Rapids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Primary + acti­vated</td>
<td>Manchester</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Digested</td>
<td>Grand Rapids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Digested</td>
<td>Manchester</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Solvent—mixture of 50 per cent of light petroleum + 50 per cent of ethyl ether.
† Refers to—samples of light petroleum (boiling point 40–60°C).

Composting of sewage sludges with such materials as grass, straw, and household refuse, has been suggested as a means of converting sludge into a valuable fertilizer (see references 167–172). Fears have been expressed that the use of sewage sludge as a fertilizer
might spread disease (see above, and also Chapter 8). One advantage of composting, however, is that a temperature of about 160°F is reached in the compost heap if the process is properly conducted and so the resulting manure should be free from harmful organisms. The dual disposal of sewage sludge and household refuse by composting to form an organic manure has been successfully carried out in this country at Maidenhead, Leatherhead, and Kirkcudbright (Dumfries). At Maidenhead, the demand for compost has exceeded the supply. The method not only provides a solution for the dual disposal of two waste products and satisfies the many agricultural experts who consider that organic refuse should be returned to the land but also meets the public demand for the abolition of the unsightly, insanitary and unhygienic refuse tip. BURKE, however, considers that composting is only suitable as a method of refuse and sludge disposal for comparatively small areas. A recent Government report, whilst admitting that composts have definite value especially in horticulture, concludes that the 'composting of household refuse and liquid sewage sludge by local authorities appears to be generally uneconomic'. Information about fully mechanized composting plants is still somewhat meagre. Recently, however, a successful mechanical composting plant—the first of its kind in Britain and likely to be the forerunner of many similar ones—has been opened in Edinburgh. It is based on the Dano system (a Danish process) in which by circulating air into the rotating mixture of wastes and sewage

### Table 90. Analysis of sludge-cakes (dried at 100-105°C) obtained by filtration on semi-scale Dorr-Oliver filter of Manchester (Dorehams) sewage sludge conditioned with chemicals (see references 131, 132)

<table>
<thead>
<tr>
<th>Source of Sludge-cakes</th>
<th>Coagulant Used</th>
<th>Analysis on dry basis: percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Organic and Soluble Matter</td>
</tr>
<tr>
<td>Activated sludge</td>
<td></td>
<td>71.0 6.0 3.8 0.4 14.1 7.5 3.7</td>
</tr>
<tr>
<td>Activated sludge</td>
<td></td>
<td>70.4 6.0 3.8 0.3 12.1 7.5 3.7</td>
</tr>
<tr>
<td>Primary + activated sludge (1:1 by volume)</td>
<td></td>
<td>75.2 4.4 2.8 0.1 8.7 21.8 30.3</td>
</tr>
<tr>
<td>Primary sludge*</td>
<td></td>
<td>75.8 3.1 2.3 trace 7.0 30.3</td>
</tr>
<tr>
<td>Elutriated digested sludge†</td>
<td>Activated</td>
<td>60.1 3.5 3.8 0.06 11.6 8.7</td>
</tr>
<tr>
<td>Elutriated digested sludge†</td>
<td>Chlorinated</td>
<td>62.3 3.2 3.3 0.05 9.3 11.6</td>
</tr>
</tbody>
</table>

* Containing a small proportion of returned activated sludge.
† From mixed activated + primary sludges (1:1 by volume).
sludge, the fermentation at about 150°F is accelerated so as to take only 5-6 days. The Edinburgh plant has an output of about 20 tons per day but larger so-called ‘Dano Bio-Stabilizer’ units are possible.

The value of sewage sludge and sludge composts should not be judged merely on the basis of economic considerations or on the chemical composition in terms of nitrogen, phosphorus and potassium. Indeed, Howard and others have laid particular stress on the importance of the humus present in organic manures as a soil conditioner, for the prevention of soil erosion, and as a means of increasing the resistance of plants to disease. In S. Africa, according to Howard, great benefits to agriculture have accrued since the adoption, by over 100 municipalities, of composting as a means of converting all wastes to humus. However, it should be pointed out that some industrial sewage sludges containing toxic metals may not be suitable for composting.

Other methods
In the U.S.A., various mechanical heat dryers have been used for converting wet sludge and sludge-cake into a dry product which can subsequently be incinerated or used as a manure. At Colne Valley, Rickmansworth, the vacuum-filtered sludge is brought down to a low moisture content (5-10 per cent) by flash drying which gives a powdered sludge capable of being used either as a fertilizer, if there is a demand for it, or as a fuel to provide heat for the drying of further quantities of sludge.

At many plants, the secondary sludges (surplus activated sludge, and humus sludge), which are difficult to dry, are pumped back to the primary sedimentation tanks where a mixed sludge is produced which can be dried fairly well on drying beds or can be vacuum-filtered.

An entirely new principle in sludge dewatering has been described by Clements, Stephenson and Regan. These authors have carried out experiments showing that water readily separates from primary, digested or activated sludges by the alternate freezing and thawing of the sludges. The thawed sludges can be readily filtered giving sludge-cakes which are porous, friable and have a high solids content. It is important to note that the sludges must be subjected to complete freezing and that freezing must be fairly slow. Addition of chemicals (especially salts of the trivalent metals, such as aluminium sulphate and chlorinated copperas) before freezing, but after the sludge has been cooled to some extent, facilitates the subsequent settlement of the sludges, and it is then possible after filtration to obtain filter-cakes with a solids content as high as 30 per cent. The process has been patented.
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CHAPTER 13

ABATEMENT OF POLLUTION.
II. DISPOSAL AND TREATMENT OF TRADE WASTES

The essential approach to the problem of ridding stream waters of unendurable industrial wastes lies in the active cooperation of the industries involved.

U.S. National Resources Committee.
Report of Special Advisory Committee on Water Pollution, July 1935.

INTRODUCTION

Although some industries can adopt anhydrous processes which do not involve the use of water in any quantity, the majority of mills and factories do, in fact, utilize moderate to large volumes of water for process and other work, thus resulting in the pollution of this water to an extent dependent on the particular industry and the nature of the processes. A pollution problem is thus created since the waste waters have to be disposed of in a safe and convenient manner without endangering public health and without causing nuisance. The large water requirements of many trades and the utilization of water for power and cooling purposes were, indeed, some of the chief reasons for the establishment of so many factories and mills on the banks of rivers during the Industrial Revolution, and the cause of so many of our pollution troubles today. In order to alleviate or prevent pollution of our rivers, it is necessary to provide means for the disposal and treatment of trade waste waters.

The use of the municipal sewers for this purpose is often the best method if a conveniently sited sewer is available and if the local sewage disposal works is large enough to cope with the wastes, is not already overloaded, and not adversely affected by the wastes. As a general rule, it is cheaper to deal with industrial wastes at a well-supervised sewage works and better results are obtained than by means of separate trade waste treatment plants.

If disposal to the sewers of a local authority is not feasible or practicable, then a special treatment plant must be provided but, in general, it is not yet possible to purify every trade waste to the same high standard as is attained by treatment of sewage. Complete or even nearly complete elimination of polluting matter from most trade wastes is often difficult or expensive to achieve and it is
usually necessary to be satisfied with only partial removal of the pollutants. Even if 100 per cent purification could be achieved, the cost would in most cases be quite prohibitive. For some trade wastes there is no satisfactory and economic method of treatment at all. Nevertheless, new scientific discoveries can alter the situation considerably and the solution of many difficult trade waste problems probably only awaits intensive research work by the industries concerned or by a well-equipped organization like the Water Pollution Research Laboratory. For instance, dairy wastes, at one time considered to be very difficult to purify, can now be treated satisfactorily at a reasonable cost by alternating double filtration to give a final effluent conforming to Royal Commission sewage effluent standards. Again, cyanide waste waters, as a result of recent investigations, can be oxidized by chlorination in alkaline solution to yield an effluent safe to discharge to a fishing stream.

Before a satisfactory method of dealing with a particular industrial waste problem can be recommended, it is essential to make a thorough preliminary survey of the volumes and characteristics of the various waste waters over a sufficiently long period. General methods of treatment are available for many types of wastes and these will be discussed later in this chapter. But it must be emphasized that each trade effluent problem must be considered on its merits and the best and most economic method of treatment must be determined for each type of waste after exhaustive laboratory experiments have been carried out, followed by extensive pilot plant tests and finally full-scale plant tests. Sometimes methods which give satisfactory results in the laboratory prove to be unsatisfactory when applied on a large scale. The cost of a particular process is a factor which usually has an important bearing on the choice of treatment and a careful study should therefore be made of economic factors before embarking on the process. In any case, it is advisable for a manufacturer contemplating the construction of a trade waste purification plant to make use of the services of a consultant who specializes in the treatment of industrial wastes and is able to give the best advice on the most suitable method of treatment. The information required by the consultant or by the firm of consultants should generally include at least the following items:

(i) nature of processes and materials used,
(ii) chemical composition of the effluents, including suspended solids, total solids, permanganate value, B.O.D., pH value, alkalinity or acidity, temperature, as well as any special constituents such as oil, free chlorine, sulphide, cyanide, phenols, metallic contaminants, etc.,
(iii) maximum, minimum and average volumes of discharges in gallons per hour, and the number of hours per day during which the discharges occur. In this connection, a curve showing fluctuations in flow throughout the day is likely to provide valuable information.

Much pollution can often be abated at the source by making various process and other changes, re-use of certain waste liquors, recovery of by-products, and by careful chemical control of the processes. Thus, in some cases (e.g. coal washery effluents, and 'backwater' from paper mills), the effluents can be treated and reused in a closed cycle so that there should be no discharge to the stream. It is sometimes advantageous to segregate certain wastes to facilitate treatment or disposal. Thus, chromate wastes should be kept separate from cyanide wastes at a plating works since the former are treated by a reduction process (ferrous sulphate, or sodium bisulphite) and the latter by an oxidation process (chlorination in alkaline solution). Often it is advisable to separate strong wastes from weak wastes and treat them separately. For instance, although it might prove impracticable to deal with large volumes of dilute industrial waste waters at a sewage disposal works, it is often possible to discharge to the sewers small volumes of strong liquors balanced throughout the day, thus leaving the manufacturers the easier task of treating the larger volumes of weaker wastes. As an example of a process modification leading to an abatement of pollution, the Water Pollution Research Board¹ has reported that at many milk distributing depots the delivery churns were not properly drained before being washed with water; by installing additional drainage racks and allowing the churns to drain longer, a great reduction in the amount of milk lost in washing the churns was achieved, thus leading not only to a saving in milk but also to a reduction in the strength of the waste liquids. At one depot, the milk lost in washing was reduced in this way from 1 per cent to 0.2 per cent of the milk handled, i.e. an 80 per cent reduction in pollution load.

Lippert², in his book on the conservation of solid and liquid industrial wastes, stresses the importance of the utilisation of by-products in a world in which there is a shortage of many raw materials. A good example of the recovery of a by-product is the treatment of the strongly alkaline kier liquors obtained in paper-making by digesting straw with caustic soda; these liquors are evaporated, incinerated to destroy organic matter, and re-causti-cized for recovery of valuable caustic soda by treatment with lime. The chief requirements of any scheme of by-product recovery are that the process must be relatively cheap and must yield a product
having some market value. A deciding factor in the success or failure of such a scheme is often the economics of the process. Some examples illustrating the recovery of valuable materials from industrial waste waters are collected in Table 91.

### Table 91: Examples of the recovery of by-products from industrial waste waters

<table>
<thead>
<tr>
<th>Waste</th>
<th>Treatment</th>
<th>By-products recovered</th>
<th>References (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper making</td>
<td>Screens, ‘save alls’, or Boration</td>
<td>Paper fibre</td>
<td>3</td>
</tr>
<tr>
<td>Paper and board mill.</td>
<td>Humic acid</td>
<td>Paper fibre</td>
<td>4</td>
</tr>
<tr>
<td>Anodating</td>
<td>Ion-exchange</td>
<td>Chronic acid</td>
<td>5, 6</td>
</tr>
<tr>
<td>Cuprammonium rayon</td>
<td>Ion-exchange</td>
<td>Copper</td>
<td>6, 7</td>
</tr>
<tr>
<td>Straw processing</td>
<td>Evaporation, incineration and lime treatment</td>
<td>Caustic soda</td>
<td>9</td>
</tr>
<tr>
<td>Copper pickle liquor</td>
<td>Electrolysis</td>
<td>Copper, sulphuric acid</td>
<td>3, 8</td>
</tr>
<tr>
<td>Wood scouring</td>
<td>Scrap iron</td>
<td>Copper</td>
<td>9</td>
</tr>
<tr>
<td>Coal washing</td>
<td>Acid precipitation</td>
<td>Wood grease</td>
<td>10</td>
</tr>
<tr>
<td>Distillery and food industry</td>
<td>Settlement</td>
<td>Coal slurry</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Anaerobic digestion</td>
<td>Methane*</td>
<td>11</td>
</tr>
</tbody>
</table>

* A valuable gaseous fuel of high calorific value.

Industrial wastes are often very complex in composition and may fluctuate widely in volume and strength from hour to hour and from day to day. This is due to the effect of such variables as the type, efficiency and operating schedule of the treatment plant, the skill with which that plant is operated, the nature of the processes of manufacture carried out (e.g. whether a ‘batch’ or a ‘continuous’ type of process), the types and quantities of chemicals used, whether the discharges are continuous or intermittent, the extent to which certain liquors are re-used and certain by-products are recovered, the kind of articles manufactured, the state of trade (i.e. whether brisk or slack), and accidental factors such as leakages, spillages, failure of pumps, etc. The effect of many of these variables on the pollution load in the river may be very considerable and may cause corresponding fluctuations in the composition of the river water from hour to hour. This is illustrated by Table 92, showing changes in the composition of the Sankey Brook, Lancashire (a stream much polluted by gas liquor and other wastes) at a particular sampling point over a working day.

The methods used for the treatment of trade wastes fall into three main classes, namely physical, chemical, and biological. In some
cases, a physical method will produce a satisfactory effluent, for instance the use of sedimentation to remove suspended solids from wastes containing mineral matter in suspension. Where physical methods do not suffice, a combination of physical and chemical methods may be desirable, for instance, in the treatment of many textile wastes by flocculation with chemicals followed by sedimentation in tanks. Sometimes, biological methods may be required in addition to physical and chemical methods, as in the treatment of viscose rayon wastes (page 516). However satisfactory the methods of treatment of industrial waste waters, it must be stressed that the careful management of the treatment plant is of paramount importance, for even the best-designed and most expensive plant cannot be expected to function properly if misused, or carelessly run, or if the necessary skilled supervision is lacking.

Table 92. Analysis of Sunley Brook at Park Bridge, St. Helens, on 17 May 1955 at different times of the day

<table>
<thead>
<tr>
<th>Time</th>
<th>pH value</th>
<th>4 h permanganate value</th>
<th>B.O.D. (5 days, 20° C)</th>
<th>Suspended solids</th>
<th>Phenols (as cresols)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 a.m.</td>
<td>8.8</td>
<td>90.4</td>
<td>27.5</td>
<td>64</td>
<td>6.5</td>
</tr>
<tr>
<td>9 a.m.</td>
<td>8.7</td>
<td>112.0</td>
<td>35.7</td>
<td>106</td>
<td>7.0</td>
</tr>
<tr>
<td>11 a.m.</td>
<td>7.2</td>
<td>108.0</td>
<td>40.8</td>
<td>62</td>
<td>7.5</td>
</tr>
<tr>
<td>12 noon</td>
<td>8.5</td>
<td>94.0</td>
<td>30.9</td>
<td>213</td>
<td>5.5</td>
</tr>
<tr>
<td>1 p.m.</td>
<td>9.0</td>
<td>102.0</td>
<td>43.3</td>
<td>155</td>
<td>5.5</td>
</tr>
<tr>
<td>2 p.m.</td>
<td>9.1</td>
<td>150.0</td>
<td>113.3</td>
<td>235</td>
<td>6.0</td>
</tr>
<tr>
<td>3 p.m.</td>
<td>9.1</td>
<td>138.0</td>
<td>51.5</td>
<td>235</td>
<td>6.0</td>
</tr>
<tr>
<td>4 p.m.</td>
<td>9.0</td>
<td>112.0</td>
<td>35.6</td>
<td>263</td>
<td>6.0</td>
</tr>
</tbody>
</table>

It is not possible within the limits of a single chapter to review adequately all the methods for the disposal and treatment of trade waste waters. Indeed, whole volumes have been published on this subject in Britain, Australia, Germany, and America. It is proposed, therefore, to review the general methods available for the disposal and treatment of industrial waste waters.

METHODS OF DISPOSAL OF TRADE WASTE WATERS

DILUTION BY DISPOSAL IN RIVERS

Although a small volume of organic trade waste discharging to a large river is eventually broken down by micro-organisms, especially if nitrogenous organic substances are present, many trade wastes are resistant to bacterial action and breakdown may be very
slow, hence too much confidence should not be placed in the self-purifying capacity of a stream. Indeed, the practice of discharging untreated industrial wastes to rivers had in the past led to such evil results in Britain, particularly in Lancashire, Yorkshire and the Midlands (cf. Chapter I, page 3), that its adoption should only be resorted to in very exceptional cases. In countries where rivers are very large and the sources of pollution are widely separated, the method may have its uses in certain cases. For example, KINe and his associates19, from data obtained in an investigation of the Raritan river and the Calco Waste Treatment Plant, have suggested that factories discharging acid chemical effluents to a stream should have the right, after suitable treatment of the wastes, to make use of a reasonable and small fraction of the reserve of the river's natural alkalinity and dissolved oxygen.

LAND DISPOSAL, OR IRRIGATION

In this method, the waste is permitted to flow over a large area of suitable land with porous soil, when it slowly percolates through the soil and gradually undergoes oxidation by soil bacteria to harmless end-products. This procedure does, therefore, involve treatment as well as disposal. Care is obviously needed in dealing with toxic wastes (e.g. gas liquor) by this method, for bacterial life in the soil might be destroyed if overdosing is practised and there would then be a danger of the drainage passing to the nearest watercourse and causing pollution. Other disadvantages are the large areas of land required, the possibility of nuisance from smells, and the potential danger of contamination of underground water supplies. The method is, therefore, only of limited application in this country. It has, however, been used for the disposal of gas liquor in cases where the local sewage works is too small to take it. Work on the use of gas liquor as a fertilizer has been summarized by the Institution of Gas Engineers20 and Key21, and the results indicate that although the liquor is of value as a fertilizer, presumably on account of its high ammonia content, great care is necessary in its application since it can easily destroy broad-leaved plants and germinating seeds. The toxic effect on seeds is due to the presence of thio-cyanate. When applied to grassland, there is some scorching of the grass at first but new grass soon appears and is relatively free from weeds21. ShERRIFF22 has described experiments on the application of gas liquor to grassland and arable land, and satisfactory results were obtained in Lincolnshire using liquor containing 2 per cent of nitrogen by weight and applied at the rate of 1,500 gal. per acre. The composting of gas liquor with vegetable waste material has been reported to give a good artificial manure23.
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The spraying of land, preferably grassland or other land protected by vegetative cover, with canneries and milk processing wastes has been successfully carried out in the U.S.A. as a means of disposing of these wastes but it must be pointed out that objectionable odours may be produced if the waste liquors are permitted to become septic.

In hot countries, the high rate of evaporation makes land treatment of waste liquors much easier but more liable to cause odour nuisance.

DUMPING IN SOAKAWAY OR IN DISUSED MINE OR SHAFT

The discharge of a trade waste to a soakaway, borehole, shaft, or disused mine may seem superficially to be an attractive and cheap method of disposal of an unwanted waste. 'Out of sight, out of mind' says the old proverb. Unfortunately, however, such wastes have a nasty habit of re-appearing where they are not wanted!

Southgate quotes the case of a yellow waste containing picric acid which was discharged to a disused mine shaft and subsequently came to the surface and so found its way to a stream. The author has experience of a waste from a firm of oil distillers which was discharged for some time to an old pit shaft; eventually, however, it was found that the waste drained to a stream and it took a considerable time before the underground workings were completely free from the oily, fatty material and before pollution of the stream ceased.

In this connection, too, it must be remembered that in this country it is an offence under the Water Act, 1945, to discharge noxious effluents into the ground where there is a risk of polluting water supplies. Southgate considers that the method should never be used without first consulting a geologist or engineer with local knowledge of underground formations and water supplies.

The method of injecting into underground strata is used in the U.S.A. for the disposal of waste brine at oilfields. Lee has discussed the use of properly constructed wells for disposing of waste waters from chemical industries which may be difficult to deal with any other way. Cecil considers that it may be advisable to give some pre-treatment to wastes before they are discharged to an injection well.

DISPOSAL TO SEWERS OF A LOCAL AUTHORITY

Whenever local circumstances permit, trade wastes are disposed of by discharge into the sewers of a local authority whence they pass...
on to the sewage disposal works for biological treatment in admixture with the domestic sewage. Indeed, the Institute of Sewage Purification in a memorandum on the subject accepts that the sewage works is the best and proper place for dealing with all suitable trade wastes. This convenient method of disposal is naturally not available when the factory is too far away from a sewer or is situated in a district which is not sewered, or when the trade waste is highly bactericidal, is too large in volume or too strong in relation to the amount of domestic sewage. The success of the method depends upon the sewerage system and the capacity of the sewage works, the strength and characteristics of the particular waste, the proportion of trade waste to domestic sewage, the use of some form of pre-treatment at the factory, and upon the even discharge of the waste throughout the day.

Under the Public Health (Drainage of Trade Premises) Act, 1937 (see also Chapter 2), a manufacturer has the legal right, subject to certain conditions and safeguards, to discharge his trade wastes to the municipal sewers; the local authority fixes the terms (e.g. charges, standards for the discharges) under which the wastes may be discharged. The charge is usually a modest one and as a rule disposal to a sewer is a cheaper method for the trader than the construction and operation of a special treatment plant. If these terms seem unreasonable or if the local authority refuses to accept the trade waste, then the aggrieved manufacturer has the right of appeal to the Minister of Housing and Local Government, who sends an inspector to conduct a public inquiry into the matter. The grounds on which the appeal is made must be stated before the inquiry is held, and normally information is required by the Ministry on such matters as the following:

(i) The maximum quantity of the waste to be discharged in any day and the times during which the discharge would be made.
(ii) The average and maximum rate of discharge (gallons per hour).
(iii) Analytical data on the composition of a representative sample of the discharge, including in addition to the usual analyses any special constituents such as metals, tar, oil, sulphide, cyanide, phenols, etc.
(iv) The temperature of the discharge.

A reasonable attitude on the part of the local authority and the trader can do much to assist in arriving at a solution of the many difficult problems arising out of the discharge of trade wastes to sewers. In this connection, Mahler wisely remarks:

A municipality should not impose a regulation so strict that it cannot be complied with, neither should the industry be allowed
to introduce wastes which adversely affect the operation of a
plant or sewerage system and place an unwarranted burden on
the city taxpayers, either by increased operation costs or increased
plant construction.'

The Public Health (Drainage of Trade Premises) Act, 1937, has
been much criticized because it gives a prescriptive right to traders
who discharged effluents to the sewers before the Act came into
force and places them at a considerable advantage over those
traders who made application for consent to discharges after 1937.
As PORTHOUSE succinctly puts it:

'It seems to me completely inequitable that a trader commencing
business today should have to pay for trade effluent service,
whilst the man in business before the 3 March 1937 gets off without
payment. Both traders should be entitled to the same
service on the same terms.'

In a memorandum on the subject the Institute of Sewage Purifica-
tion reaches a similar conclusion:

'... if the 1951 Act is to be effective in fulfilling its main objective
in improving the condition of rivers, and if local authorities are
to give the best service to the nation in contributing to this end
by dealing with trade effluents at their sewage works, it is most
necessary that the whole of the effluents accepted into sewers
should be under reasonable control, including those discharged
from factories established before 1937.'

Conditions for the discharge of trade effluents into sewers have
been very fully and ably discussed in a paper by LOCKETT, and
these conditions should be clearly stipulated in all consents and
agreements made between the manufacturer and the local authority.
Such conditions are obviously necessary in order to avoid sur-
charging sewers, prevent blockage and corrosion of sewers, prevent
fires and explosions due to inflammable or explosive compounds,
stop the formation of noxious or poisonous gases or vapours in
sewers, and avoid damage to the sewage treatment plant and the
biological processes used at the sewage works (percolating filters,
activated sludge, and sludge digestion). It is particularly important
to avoid discharging anything which will block or damage the
sewers. For instance, tannery wastes contain lime, which, if not
removed by pre-treatment (e.g. treatment with flue gases or carbon
dioxide to precipitate calcium carbonate which can be settled out),
may cause the formation of calcium carbonate scale inside the
sewers by interaction of the lime and the carbon dioxide present in
the sewage. REDLICH reports that such scales have been known
to grow to a thickness of 1 in. in about a year!
It is necessary for the municipality to bear in mind that, even after the reception of trade wastes to the sewers, the final effluent discharging from the sewage works to the stream must still comply with any standards set by the river board (see Chapter 14 for a discussion of such standards).

Some of the conditions that can be imposed on traders discharging wastes to sewers will now be further discussed. In order to fulfill many of these conditions, some form of pre-treatment of the wastes may have to be adopted by the trader.

**Quantity of Waste**

Balancing of the waste may be desirable in many cases so that the quantity can be spread out evenly or discharged only during certain times of the day. If balancing is not properly carried out, there is a distinct risk of the occurrence of exceptionally high flows during the working day which might cause overflows into the storm tanks without adequate dilution.

Experience in the highly industrialized areas covered by the Mersey River Board and the Lancashire River Board has shown that difficulties in the purification of a combined flow of domestic sewage and industrial wastes by normal biological methods can be expected if the volume of the trade wastes exceeds about 50 per cent of the D.W.F. at the sewage works and it may prove impossible in such cases, without additional treatment, to obtain a final effluent satisfying the standards of the river board. With certain inhibitory trade wastes, the proportion that can be treated may be much less than 50 per cent and in the cases of a few difficult and strong wastes (e.g. kier liquors, gas liquor, distillery waste), the volume that can safely be admitted to the sewage works must be strictly limited and it may even be necessary to exclude the waste altogether from the sewers. For instance, Ward has reported the case of an exceptionally strong waste (distillery waste, obtained in the manufacture of alcohol by fermentation of crude beet molasses) which, although constituting only 0.7 per cent of the total sewage flow, upset the biological treatment of the sewage by the activated sludge (bio-aeration) process to such an extent as to make purification economically impossible. Eventually, the firm concerned was persuaded to remove to the coast and to discharge the waste into an estuary. Again, it is generally accepted that the maximum amount of spent gas liquor that can be dealt with satisfactorily at a sewage works having a reasonable reserve of purification capacity is 0.5 per cent by volume of the flow at the sewage works. In practice, this means that a sewage works can usually just deal satisfactorily with the gas liquor from a gas works serving approximately the same population. In this connection, Pickering has sounded a
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note of warning by pointing out that the centralization which is going on in this country under nationalization might mean that in certain districts the volume of gas liquor produced might exceed the normal amount and in some cases might even reach as much as 2 per cent of the D.W.F. of sewage, i.e. four times the maximum quantity of spent liquor stipulated above. Such a large proportion of gas liquor would have an adverse effect upon biological purification processes and it might become necessary to dispose of part of the liquor in some way other than by discharge to the sewers.

Acidity and alkalinity

Strongly acid or alkaline wastes should be neutralized before discharge to the sewer not only to prevent corrosion of sewers and jointing materials and to avoid the liberation of toxic gases (e.g. by interaction of acids and such substances as sulphides and cyanides) but also because biological processes of sewage purification work best in the region of neutrality (i.e. at about pH 7·0). When the sewage works is comparatively small and the waste is strongly acid or alkaline, neutralization should be carried out to within fairly narrow pH limits (say, between pH 6·0 and 8·0), but a wider range (e.g. 6·0-10·0) is permissible at a large sewage works where there is ample dilution and plenty of available buffer capacity.

Many workers have made interesting observations on the effect of pH on the biological treatment of sewage. BREEDHAM showed that treatment of Bradford sewage containing wool-scouring wastes on percolating filters, or in laboratory experiments with activated sludge, gave the best results at pH 6·0-6·5; at pH 4·0 results were not nearly so good, the adverse effect of pH on purification being more marked with activated sludge treatment than with biological filtration. LUMB also found that activated sludge was most efficient in treating Halifax sewage at pH 6·0-7·0, the optimum pH value being around pH 6·5. WRIGHT found that the activated sludge process was adversely affected by acid conditions (pH 5·0-9 or less). WOOLDRIDGE and STANDFAST, in laboratory experiments on the oxidation of activated sludge-sewage mixtures using the Barcroft differential manometer, found that oxidation proceeded best at pH values between 7·0 and 8·0 but there was little loss in efficiency when the pH fell to 6·0 or rose to 9·0. There was, however, marked loss in efficiency outside these values, i.e. below 6·0 or over 9·0. CUONG, working at the activated sludge plant at Kyoto City, Japan, where the sewage contains a large proportion of dye wastes, found that the efficiency of the activated sludge process was affected when the pH was about 8·0. Sewage having a pH of approximately 9·0 was brought down to about pH 7·0 with carbon dioxide (using exhaust gas, containing 5-10 per cent of...
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CO₂, from gas engines burning sludge digester gas), this enabled the aeration period and amount of air required to be reduced and resulted in an improved final effluent. The use of carbon dioxide for rendering alkaline sewages more amenable to biological treatment has been the subject of an American patent. Goldthorpe reported that two high-rate percolating filters at Huddersfield treated sewage varying in pH from 3.0–9.0, and had worked at pH 3.5 for 3 hours and at pH 9.0 for 2 hours without showing any harmful effects. Summarizing, it can be stated that the biological treatment of sewage mixed with trade wastes is best carried out between pH 6.0 and 8.0, and that there may be marked loss in efficiency, particularly with the activated sludge process, outside these limits.

Organic content

It is often necessary to stipulate a maximum permitted figure for the amount of organic impurity in the trade waste in order to avoid too great an overload on the sewage works. The quantity of organic matter is usually assessed on the basis of the 4 hours permanganate value, the B.O.D.,* or the McGowan strength figure. Where trade wastes admitted to the sewers have a high content of organic matter, it is important that provision should be made at the sewage treatment plant for the disposal of the larger volumes of sludge likely to be produced (e.g. extra sludge drying beds or extra capacity in the sludge digestion plant). Jenkins states that the normal amount of sludge produced from domestic sewage, i.e. about 50–60 lbs. of dry matter per head of population per year, may rise to over 100 lb. when trade wastes are present.

Suspended solids

Some limit must be placed on the amount of suspended matter in a trade waste in order to avoid the deposition of solid matter in the sewers with possible eventual blockage. A reasonable limit is 200–400 p.p.m. but this figure must depend to a large extent on the proportion of trade waste to sewage, the size of the sewers, the flow in the sewer and on the character of the suspended matter. Lockett considers that with a good flow of sewage and suspended matter flocculent in character, 800 p.p.m. of suspended solids could be permitted in the trade waste, or, in the case of large sewers, 1,400 p.p.m. Settlement tanks, or catchpits, can be used for the removal of suspended solids from trade effluents.

* B.O.D. is not a good guide except in cases where the wastes are somewhat similar in composition to sewage and free from inhibitory substances. Indeed in some cases (e.g. gas liquor) the B.O.D. can be very misleading.
ABATEMENT OF POLLUTION II

Sulphides

Many authorities (e.g. Manchester Corporation) insist on the removal of all sulphide from discharges to sewers in order to obviate the possibility of the evolution of poisonous sulphuretted hydrogen (H\textsubscript{2}S) which has been known to cause fatalities to men working in the sewers. Lockett\textsuperscript{35} has suggested that a limit of 50 p.p.m. of sulphide (calculated as S) could be safely allowed in cases where the discharge is small in volume and less than one quarter of the flow of sewage in the sewer.

Grease and oil

Lockett\textsuperscript{35} gives a permissible limit of 400 p.p.m. for grease and oil, since these materials if present in excessive quantity not only foul mechanical and other equipment at a sewage works but also materially interfere with biological purification processes. Manchester Corporation has recently set a maximum limit of 400 p.p.m. for oil plus suspended solids in wastes going to the sewers. Solid fatty matter has been known to choke small sewers. Insoluble oil and fats should be removed by some form of grease trap. "Soluble" oils should be segregated and given chemical treatment (see page 502) so as to separate and ultimately remove the oil.

Cyanides

Cyanides, on account of their toxicity to bacteria, can upset biological processes very considerably. It has been shown by Lockett and Griffiths\textsuperscript{47} that when more than about 1 p.p.m. of cyanide (expressed as HCN) is present in sewage, interference with the biological treatment of the sewage by activated sludge begins. A similar figure is given by Eldridge\textsuperscript{15}. Pettet and Thomas\textsuperscript{48} concluded from experiments with percolating filters that the concentration of cyanide in sewage treated in filters should not be greater than 1-2 p.p.m. (expressed as HCN). The amount of cyanide in the waste discharged to the sewer can, of course, exceed this amount because of dilution but should not as a rule be greater than about 10-20 p.p.m. on account of the possibility of the liberation by acids of volatile hydrogen cyanide sufficient to kill men working in the sewer.

Toxic metals

Many workers have shown that the compounds of the heavy metals, such as lead, copper, nickel\textsuperscript{49} and chromium\textsuperscript{50, 51} (especially in the form of chromate) have an adverse effect on the treatment of sewage by biological processes when present in sewage in amounts above about 1-3 p.p.m. Moreover, these metals usually tend to
become concentrated in the sludge in the sedimentation tanks and this can lead to a marked decrease in the efficiency of the sludge digestion process (see Chapter 12, page 465). SHEPP and ZIEGLER suggest that, in order to avoid interference of zinc with such sewage treatment processes as biological oxidation and sludge digestion, the discharge of zinc wastes to the sewer should be regulated so that the content of zinc in the sewage is not more than 5 p.p.m.

Gas liquor
The discharge of crude ammoniacal gas liquor to the sewers should as far as possible be avoided. The high ammonia content of this liquor as well as the presence of cyanide and sulphide may cause difficulties with the subsequent biological treatment and may present hazards to men working in the sewer due to evolution of toxic gases (e.g. ammonia, hydrogen cyanide, and hydrogen sulphide). If, however, the crude liquor must be accepted, then, as stated in a memorandum of the Institute of Sewage Purification, the liquor must be completely free from tar and not more than 0.25 per cent by volume should be admitted to the sewage works. Spent gas liquor, from which much ammonia and most of the cyanide and sulphide have been removed in a concentrator plant, is rather easier to purify by biological processes than crude liquor, and can generally be admitted to the sewage works in amounts up to about 0.5 per cent by volume of the D.W.F. of the sewage. However, it is difficult to lay down any hard and fast rule about the volume of gas liquor that can be dealt with at a sewage works and much will depend upon local circumstances, such as the character of the sewage (i.e. whether domestic or industrial), the reserve of purification capacity, and the strength and composition of the gas liquor. The quantities of gas liquor discharged should be carefully regulated so as to avoid sudden flushes of strong liquor which may damage filters or even put out of action an activated sludge plant. The difficulties of treating gas liquor at a sewage works are accentuated by the presence of high and inhibitory concentrations of monohydric and polyhydric phenols in both the crude and spent liquor, the higher phenols (or "tar acids") being particularly resistant to biological oxidation. Unless a sewage works has a large reserve of purification capacity—a most unlikely contingency in these times—it will be necessary to provide extra capacity (i.e. additional filters or aeration units) to deal with the gas liquor. In order to calculate the additional filter capacity required to deal with gas liquor at a sewage works, it can be taken that, following the suggestion of GARNER, an extra 1 yd. of filter should be provided for every gallon of spent gas liquor having a 4 hours N/80 permanganate...
value of about 12,000 p.p.m. It is assumed that the proportion of the spent liquor to be treated with the sewage does not exceed 0.5 per cent by volume of the D.W.F. of the sewage. If a weaker gas liquor is being treated, naturally the extra filter capacity can be proportionately less. For instance, if the gas liquor has a 4 hours permanganate value of 6,000 p.p.m., only ½ yd. of filter should be allowed for each gallon of liquor.

Most of the larger authorities in this country accepting considerable quantities of industrial wastes into their sewers have a very efficient organization for the inspection and control of such discharges. A municipality can charge a trader for the treatment of trade wastes accepted into the sewers, the rates of payment varying from a few pence to several shillings per 1,000 gallons depending on the strength and nature of the waste. At the West Middlesex (Mogden) Sewage Works, the following formula has been used for certain trade wastes as a basis for fixing a charge for admission of the wastes to the sewers:

\[
\text{Charge (in pence per 1,000 gal.)} = 1 + \frac{M}{75} + \frac{S}{60}
\]

where \( M \) = McGowan strength (page 419) of the settled waste, and \( S \) = suspended solids in parts per 100,000.

It should be remembered that this formula may require modification to suit present-day costs and, moreover, is only applicable to cases where the cost of treating sewage is similar to that at Mogden.

Under the Public Health (Drainage of Trade Premises) Act, 1937, however, a manufacturer discharging a waste before 3 March 1937 is exempt from any charges provided that the nature or composition of the waste has not altered since that date and that the quantity of effluent discharged to the sewers is not greater than that discharged during the year ending 3 March 1937. Laundry waste is not regarded as 'trade waste' for the purposes of the 1937 Act and it can be discharged to the sewers without the consent of the local authority but by-laws limiting the temperature and pH value can be made.

Those interested in the American approach to problems of handling trade wastes by municipalities should consult the report of the 1945 Committee on Industrial Wastes of the California Sewage Works Association and a paper on the determination of fair sewage service charges for industrial wastes by Schroepper. Special formulae used by various cities in the U.S.A. for calculating the charges to industries sending wastes to the public sewers are reviewed critically by Symons and by Besseleyvre.
Many manufacturers producing highly polluting trade effluents (e.g. distillery waste, sulphite waste liquor, coke oven effluents and noxious chemical wastes of various kinds) have found it convenient to set up their factories on tidal waters or estuaries into which they can discharge their wastes. Tidal waters do not normally come under the jurisdiction of a river board in England and Wales and consequently these traders do not have to conform to any restrictions which would be imposed under the Rivers (Prevention of Pollution) Act, 1951, if their factories were sited on an inland stream. It should, however, be emphasized that in the 1951 Act, provision exists for an extension of the Act to cover tidal waters (see below). Sea-water tends to be somewhat alkaline in reaction (pH value usually around 8-2-8-4) and so may be suitable for neutralizing acidic chemical wastes. It must, however, be remembered that perfect mixing rarely occurs in practice and that there may be little dilution available at low tide. Moreover, the view sometimes expressed that the water in a polluted estuary goes out to sea on the ebb tide and is replaced by unpolluted sea-water on the flood tide is now known to be erroneous. It is only in those estuaries that are short and steep that polluting matter is easily carried away by the tides. In practice, then, the discharge of untreated trade effluents into many of our estuaries has led to increased pollution within recent years, resulting in much and increasing fish mortality, and is to be strongly deprecated. As far back as 1935, Alexander, Southgate and Bassindale8 reported that every year large numbers of salmon and sea trout smolts were killed in the polluted Tees estuary when they migrated through the pollution barrier. The most toxic trade wastes discharged to this estuary were spent acid pickle liquors and coke-oven effluents. Evidence collected during fish migration in 1931 suggested that the main cause of fish mortality that year was the cyanide (derived from coke-oven effluents) which was present to the extent of about 0-2 p.p.m. (expressed as CN) or more—sufficient to kill fish in quite a short time. It is evident that if fish life in our estuaries and the fishermen who depend for their livelihood on fishing are to be adequately protected, then serious consideration should be given by traders to some form of pre-treatment for all noxious and poisonous effluents before discharge to estuarial waters.

It would appear that one way to obtain some control over trade effluents discharging to estuaries would be to secure an extension of certain provisions of the 1951 Act to tidal waters. Although this can be done by applying to the Minister of Housing and Local Government for an order, under Section 6 of the Act, it is doubtful
whether the Minister would encourage such an application if it involved much capital expenditure on extensions to a sewage works to enable the works to receive and deal with trade effluents satisfactorily.

**GENERAL METHODS OF TREATING TRADE WASTE WATERS**

**PHYSICAL METHODS**

*Sedimentation*

Sedimentation, or settlement in tanks or lagoons to remove settleable solids by gravitation, is the oldest and most widely used of all the methods for purifying trade wastes, and plays a vital part in the treatment of almost every type of waste. Indeed, in many cases (e.g. waste waters from sand washing or from a coal washery) settlement is often all that is really necessary to give a satisfactory effluent fit for discharge to a stream. Tanks should be frequently cleaned and the accumulated sludge removed. If the sludge is allowed to accumulate, it may become septic and not only will inferior effluents be obtained but also the capacity of the tanks will be reduced. The majority of trade waste slurges have no commercial value and after drying on beds are generally disposed of by tipping on to waste ground. In a few cases, however, the solid matter removed (e.g. coal slurry) may have some commercial value. When continuous flow tanks are used, the velocity of flow must be low enough to permit satisfactory settlement of the suspended solids; provision can be made in continuous flow units for the removal of sludge by mechanically operated scrapers. The provision of tanks of the type which can be de-sludged easily while they are in operation is much to be preferred, as these rule out the necessity of putting a tank out of action for cleaning (thus reducing settling capacity) and make the de-sludging less objectionable to the workmen.

The suspended matter in some industrial wastes does not always settle easily because the particles may be in a very finely divided state. In such cases, preliminary treatment by mechanical flocculation (page 498) or by chemical flocculation (page 509) may be necessary before sedimentation.

*Balancing or equalization*

Trade effluents not only show variation in composition according to the particular industry but even the same trade (e.g. textile dyeing and finishing, organic chemical wastes) can produce effluents which vary widely in volume and composition from day to day and
even from hour to hour. In such cases, the provision of balancing tanks (capable of holding at least a day's supply of wastes) to even out, equalize and mix the various effluents can be advantageous.

**Mechanical flocculation**

Mechanical flocculation, or slow stirring by means of revolving paddles (see Chapter 12, page 427) causing finely divided solids to coalesce to give larger flocs which settle more readily in tanks, has found some use in the treatment of sewage. It deserves more recognition as a means of trade waste treatment than it has hitherto received and can advantageously be used in conjunction with chemical flocculation. The return of some of the settled sludge to the flocculator can in many cases prove beneficial.

**Mechanical filtration**

Among the most useful and important methods for removing the coarser solids from trade wastes, prior to settlement, is screening. The screens may range from coarse bar screens (openings about 2-4 in. in width) to fine screens (apertures about 0.02 in. or less). All types of screens require frequent cleaning.

A recent development, which promises to be a valuable method of removing fine suspended matter from trade wastes in special cases where other methods (e.g. sedimentation) do not give a satisfactory effluent, is the use of micro-strainers of very fine mesh (aperture about 20 \( \mu \) in diameter). These have already been mentioned in connection with the treatment of sewage effluents (page 457). Their use in water treatment is well established.

Vacuum filters are used chiefly to remove the somewhat coarse suspended material from certain waste waters (e.g. fibrous material from paper making wastes). Their use in connection with the filtration of sewage sludge previously conditioned with chemicals has been discussed in a previous chapter (page 462).

Straining filters used at atmospheric pressure and consisting of beds of coke, sand, or other similar material are often used for removing suspended solids from trade wastes. Pressure filters, which are much used in the field of water treatment, only find occasional use in the treatment of trade wastes.

**Evaporation**

On account of high fuel costs, evaporation is an expensive method of treatment used only in special cases, for example, for radioactive wastes and certain concentrated wastes having a high organic content.

Thus, evaporation has been employed at the Knolls Atomic Power Laboratory, U.S.A., for concentrating laboratory, laundry and other dilute radioactive waste waters; the concentrated liquor
can be further dried on drum dryers and then stored in shielded stainless-steel drums.

Evaporation is used for the treatment of sulphite cellulose waste liquor obtained in the manufacture of paper pulp by the digestion of wood chips with solutions of sulphites (usually calcium bisulphite). The liquor is of a very grossly polluting character, being acid and having a 4 hours permanganate value of 10,000-70,000 p.p.m. The evaporated product finds a number of commercial applications in this country, for instance, as a road-binding material, for moulding sand, for tanning purposes, and for the production of insecticides and fungicides. When the market for these products is limited, as in the U.S.A., the evaporated liquor (containing 50-60 per cent of solids) can be incinerated by spraying into the top of a cyclone furnace at the rate of 4-5 gal./min. Corrosion-resistant equipment is necessary when evaporating sulphite cellulose waste liquors. Difficulties also arise owing to the deposition of large amounts of calcium sulphate on the heating surfaces thus necessitating interruptions for cleaning. One way of overcoming this difficulty involves the use of the patented Rosenblad evaporator which operates in several mills in the U.S.A. In this evaporator, flat plates (instead of the usual heating tubes) are arranged vertically at equal distances so as to give an even number of channels. Steam passes down through one channel whilst the waste liquor to be evaporated passes upwards through the next channel and so on. By the alternate use of the two sets of channels in this way, any deposits left by the waste are effectively removed by the steam.

Evaporation, followed by incineration to remove organic matter and treatment of the ash with lime to give caustic soda, finds some use for the treatment of the grossly polluting liquors and the stronger wash waters obtained when paper pulp is prepared by digesting straw, cotton linters and waste cotton with caustic soda in 'Kiers'. Valuable alkali is thus recovered in these 'caustic soda recovery plants' and much organic matter which would otherwise pollute the river is removed.

Sulphuric acid can be recovered from the spinning bath waste acid liquors, obtained in the manufacture of viscose rayon, by evaporating the filtered wastes and crystallizing to remove sodium sulphate and other salts.

Adsorption

Adsorption, or the adherence of a substance, usually in solution, to the surface of another material, is sometimes of great value as a means of purifying trade wastes. Indeed, it plays an important role in the widely used process of chemical flocculation (see page 509) in which precipitates of metallic hydroxides (especially those of
aluminium and iron) are formed in situ by the interaction of suitable chemicals and absorb unwanted impurities from the liquor.

An important adsorbent is activated carbon, small doses of which are used for the removal of tastes and odours from public water supplies. Carbon has only found occasional use in the treatment of trade wastes since it is expensive, the amounts required are rather large, beds of the material may occupy an extensive area, regeneration is sometimes difficult or impracticable, and there might be the problem of the disposal of any spent regenerant solution. Snell 66 showed that coloured wastes from the dyeing of silk could be decolorized by the use of the somewhat large amount of 6 lb. of carbon per 1,000 U.S. gallons (about 720 p.p.m.) but the carbon could be re-used several times before re-activation was necessary. Rudolf 67 and Hanton 67 showed in laboratory experiments that large amounts of powdered activated carbon were required to remove colour from effluents obtained by the biological treatment of rag cooking liquor, gum wastes, and yeast wastes with activated sludge; chlorine was found to be much more efficient for colour removal. Activated carbon filters were at one time used at the Tingley Gas Liquor Treatment Plant (see page 523) for the removal of the last traces of phenolic bodies from the effluent but they were too expensive owing to the necessity for the frequent renewal of the carbon. Activated carbon has recently been used 67A for the pre-treatment of the strongly bactericidal wastes from a chemical factory manufacturing various pesticides and insecticides; the treated wastes were then amenable to biological treatment on percolating filters. Granular activated bauxite and granular fuller's earth were used by Thornton and Moore 68 in laboratory experiments on the adsorption of various types of dye used in dye manufacture or in dyeing textiles. Some of the dyes were easily adsorbed, others were adsorbed with difficulty or not at all. In general bauxite was found to be superior to the cheaper fuller's earth as an adsorbent and the best results were obtained with high initial dye concentrations. The adsorbents could be regenerated by heating to 1,100°F, or, if recovery of dye is desired, by extraction with solvents or salt solutions.

Experiments on the removal of radioactivity from tap water containing various radioactive contaminants 69 showed that stirring for 13 hours with slurries of powdered metals, especially iron (100 p.p.m.), was an effective method of removing most of the radioactive isotopes by adsorption on to the metal surface.

Extraction with solvents

Solvent extraction only finds limited application in the treatment of trade wastes, but has, however, been used for the recovery of
phenols from ammoniacal liquor produced at a gas works. Among the solvents used for the extraction of the phenols are benzene ("benzole"), light tar oil, tricresyl phosphate and aliphatic esters (e.g. phenoxyvan, a mixture of esters, but chiefly isobutyl acetate). The phenols are recovered from the extracts by distillation or by treatment with caustic soda\(^1\), 18, 70, 71.

Southgate\(^3\) reports that on the Continent and in the U.S.A. wool is sometimes subjected to a preliminary extraction with organic solvents to remove most of the grease, and when the degreased wool is afterwards scoured by a wet process the wastes are much less polluting than those obtained by the usual scouring processes.

Dialysis

Dialysis is rarely used in the treatment of trade wastes and finds its chief use in the treatment of the alkaline liquors obtained in the manufacture of viscose rayon. These waste alkaline caustic soda liquors are dialysed to remove dissolved hemicelluloses and the caustic soda so recovered can be re-used\(^65\).

Electrolysis

Electrolysis is another process rarely used in trade waste treatment, presumably on account of the expense. A good example of the successful application of electrolysis is the recovery of copper from spent pickle liquor obtained when copper is treated with sulphuric acid to remove scale. This liquor contains copper sulphate and on electrolysis gives copper (which is deposited at the cathode) and sulphuric acid\(^1\).

\[
2\text{CuSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + 2\text{H}_2\text{SO}_4 + \text{O}_2
\]

Southgate\(^3\) considers this to be the best method for treating pickle liquor at copper mills of medium or large size since valuable copper and sulphuric acid are recovered and can be re-used.

Flotation

Flotation is a method whereby matter in suspension, which does not settle by gravity, is caused to rise to the surface of the liquid by the application of aeration, vacuum, or other device, especially in the presence of a surface-active chemical. So-called 'froth flotation' has been used for the recovery of fine
material from coal washery waste waters which may contain coal
dust (including very fine particles difficult to settle), shale, clay,
sand, pyrites, gypsum and other mineral substances. In one
method, the waste waters are agitated with a little oil (e.g.
pine oil) and aerated to produce froth containing fine coal dust
which is removed and dewatered on a vacuum filter.

Experiments by Eliasen and Schulhoff on the treatment of
laundry waste have shown that good removals of B.O.D. and grease
can be obtained by a combination of chemical precipitation and
flotation. The waste is treated with a flocculating agent (e.g.
aluminium sulphate), aerated for 5 minutes and then a vacuum
(15 in. of mercury) applied for a further 5-15 minutes whereby
tiny gas bubbles are generated causing the flocs containing adsorbed
impurities to rise to the surface.

Gibbs has given an account of pilot plant studies on the use of
flotation for removing fibre and filler from white water wastes at a
paper mill, and for the recovery of grease and fatty acids from wool
scouring and soap wastes. A large-scale plant dealing with soap
wastes in this way gave removals of fatty acids exceeding 96 per
cent and a final effluent containing only about 10 p.p.m. of fatty
acids.

Oil separation
Some waste waters (e.g. oil refinery wastes, oily floor washings from
engineering works and garages) contain considerable amounts of
oil and would cause pollution of streams if discharged without some
form of treatment. The usual method of dealing with this type of
waste is to settle by gravity in an oil-water separator or interceptor
of special design, when in many cases the oil floats to the surface
and is removed by the use of skimming devices.

Gravity separators cannot be directly used for oil-water emulsions
and for so-called ‘soluble oils’ (page 24) without first breaking the
emulsions by the application of such chemical methods as addition
of sodium chloride or acid and flocculation with calcium chloride
or with aluminium sulphate.

Oily and greasy matter can sometimes be removed from trade
wastes by aeration followed by the skimming of the oily scum from
the surface.

Centrifuging
The centrifuge has found some application in the treatment of wool-
scouring waste liquors for the removal of wool grease, which
has a high market value on account of its lanoline content. According
to Smits, the use of a centrifugal separator of special design
(the Adams machine) removes about one half of the greasy material
from a waste containing 3-5 per cent of grease; this removal is much less than that obtained by the more popular 'acid cracking process' and consequently the resulting effluent is not satisfactory for discharge to a stream.

**Volatilization**

This process is occasionally used to remove volatile pollutants from waste waters and is generally carried out by passing steam through the hot liquors ("steam stripping"). Thus, at the Hamilton plant of the Armco Steel Corporation, New Miami, U.S.A., phenol is recovered from coke oven waste waters by blowing steam through the hot ammoniacal liquors and absorbing the volatilized phenol in hot caustic soda solution. Steam can be used in a similar way to remove carbon disulphide from viscose rayon wastes.

Gases (e.g. hydrogen sulphide, present in the free state or as sulphide) and volatile liquids (e.g. hydrogen cyanide, present in the free state or as cyanide) can be removed from trade wastes by aeration at the proper pH value (say, pH 5-6).

**Electro-dialysis**

Electro-dialysis, or dialysis through a membrane (e.g. tile, parchment, asbestos, etc.), caused by the passage of an electric current, is usually carried out in a cell divided by two membranes into three compartments. No large-scale applications have so far been reported. Laboratory experiments using electro-dialysis have been described by Bonacci and Rudolfs for the treatment of distillery wastes from molasses fermentation, and by Rudolfs and Tritternick for dealing with wastes produced in the manufacture of compressed yeast, but the results obtained in these experiments were not particularly satisfactory.

**Freezing**

This process has already been mentioned in the chapter on sewage treatment in connection with the dewatering of sewage sludges (see Chapter 12, page 470). Honson has reported that freezing has been used at a plant in the U.S.A. for the de-greasing of raw wool (prior to scouring with soap) by cooling to -37°C to -51°C and beating the wool to separate the solidified grease. Although a 48 per cent removal of grease is effected, a disadvantage is that the quality of the wool is adversely affected by the freezing.

**Ultrasonic (or supersonic) waves**

These waves may have possible uses for sterilization, for the prevention of boiler scale, and for increasing the rate of settlement of suspended matter in a liquid. Lyon claims that exposure to...
ultrasonic vibrations does actually improve the settleability of activated sludge but this is denied by HUSMAN83K who reports unfavourable effects of the waves on the sludge (e.g. conversion to a fine suspension, and interference with the purifying capacity).

Aeration
Aeration is sometimes a valuable method of dealing with trade wastes and examples of its use have been given under the headings of oil separation (page 502) and volatilization (page 503). It is also a useful and necessary adjunct in certain chemical flocculation processes, for instance treatment with copperas and lime (see page 510) where it not only assists mixing but also oxidizes ferrous hydroxide to ferric hydroxide.

CHEMICAL METHODS
Chemical methods for the treatment of industrial waste waters are second in importance only to physical methods. GURNHAM84 in a discussion of some of the chemical engineering aspects of industrial waste treatment has reviewed the most useful chemical methods available and these include neutralization, oxidation, reduction, double decomposition and ion exchange. Some examples of the application of these methods will now be given.

Neutralization
This method is used when acid or alkaline wastes are encountered. In general, such wastes should be neutralized so as to bring them within the pH range 5·0-9·0 or in some cases even 6·0-8·0. Where acid and alkaline wastes are produced at the same works, they can be used for mutual neutralization but it is rare that the amounts of wastes produced are such that they exactly neutralize each other. Alkaline wastes are generally neutralized with sulphuric acid and acid wastes with lime, these two compounds having the advantages of being relatively cheap and easily available in large quantities. A disadvantage of the use of lime for neutralizing acid wastes containing sulphuric acid is that sparingly soluble calcium sulphate is produced and this deposits as a voluminous white precipitate which necessitates the provision of sufficient settling tank capacity and creates an awkward sludge disposal problem. For these reasons, the more expensive soda ash (sodium carbonate) is sometimes used for neutralizing sulphuric acid as no sludge is then produced. Beds of limestone, although satisfactory for neutralizing hydrochloric acid (which forms a very soluble calcium salt), are less suitable when sulphuric acid is present as a deposit of sparingly soluble calcium sulphate soon reduces the effectiveness of the beds. GEHM85
however, using experimental up-flow beds of fine limestone, claimed that sulphuric acid could be neutralized satisfactorily to pH about 4.2 if the acidity did not exceed 5,000 p.p.m. (expressed as CaCO$_3$); the best results were obtained using limestone 1-2.5 mm in diameter in beds 2-4 ft. deep with up-flow rates of 20-80 U.S. gallons per square foot of bed per minute.

HOAK$^{86}$ has given a useful summary of the characteristics of a number of suitable alkaline reagents for neutralizing acid iron pickle liquor (which contains ferrous sulphate and sulphuric acid) and has discussed critically important considerations in the selection of a neutralizing agent such as cost, alkalinity, reactivity, and settling characteristics of the sludge. Quicklime (properly slaked and wetted before use) is generally used for these waste liquors but dolomitic lime is less suitable owing to its somewhat low reactivity. Caustic soda is the most reactive reagent but its high cost normally precludes its use unless a cheap waste source is available. LAB$^{87}$ has described a plant suitable for neutralizing iron pickle liquor with lime. Experiments by the Water Pollution Research laboratory$^{88}$ on the neutralization of iron pickle wastes suggest that, to avoid the production of a bulky sludge difficult to dewater, the liquors should be neutralized so that the iron sludge is gradually precipitated and this can be achieved by the use of precipitated calcium carbonate, or a lime sludge from a waterworks, followed by aeration.

Advice on the handling and method of application of various liming materials suitable for neutralizing acid trade wastes is given by LEWIS and YOST$^{89}$ who emphasize that lime should be properly slaked and applied in the form of a slurry and that sufficient time should be allowed to permit proper interaction between the lime and acid. Where sulphuric acid wastes are being handled, it is recommended that dolomitic limestones (which have a high magnesium content) should be used for neutralization so as to keep sludge formation at a minimum.

The control of neutralization on a large scale is best carried out by the use of pH recorders; these automatically operate a valve which is fitted to a feeder tank for adding acid or alkali.

Many examples are recorded in the literature of the use of carbon dioxide for neutralizing alkaline trade wastes. Two cheap sources of carbon dioxide are available in (a) flue gas, which contains about 12-18 per cent of carbon dioxide$^{90}$, and (b) sewage sludge digester gas, which can be burnt to give carbon dioxide. The Royal Commission on Sewage Disposal$^{12}$ in their 9th Report suggested that cotton kier liquors might be neutralized with carbon dioxide. COPSON and CURTIS$^{91}$ used flue gas for neutralizing strongly alkaline cotton kier liquors to the bicarbonate stage, then
added untreated kier liquor to convert bicarbonate to carbonate, and finally precipitated with calcium chloride thereby reducing the colour and organic content by 75-80 per cent and giving an effluent of pH value 7.8-8.5. Flue gas and carbon dioxide have been used for the neutralization of the spent waste liquors resulting from the washing of light petroleum oils with caustic soda. RUFFERBORG and ALLISON reduced the pH value of tannery wastes to 6.4-6.7 by means of flue gas, and treatment was completed by adding lime until the liquor was slightly alkaline to phenolphthalein; repetition of this treatment was then carried out on the settled liquid. McCARTHY has described pilot plant studies on the treatment of alkaline wool-scouring wastes with carbon dioxide to reduce the pH value to about 8.0 and treatment was completed by coagulation with calcium chloride. The alkalinity of laundry wastes can be much reduced by means of carbon dioxide and further purification can then be achieved by coagulating with aluminium sulphate. A large firm of paper manufacturers near Manchester have recently carried out successful pilot plant experiments using flue gas (obtained by the combustion of a special fuel oil) to neutralize the high alkalinity of the firm's trade waste, and a scheme for a full scale plant is now being investigated. It must be noted, however, that the use of flue gas obtained from the combustion of coal might well mean the installation of scrubbing devices to remove phenols, etc.

Chemical oxidation Although chemical oxidizing agents (e.g., chlorine, chlorine dioxide, ozone) have been in fairly common use for many years for the sterilization of potable water supplies, their employment in the field of industrial waste treatment has been somewhat limited. Perhaps the most striking modern example of the successful application of oxidation on a commercial scale is the destruction of cyanides in electroplating wastes and wastes from the case-hardening of steel by chlorination in strongly alkaline solution (pH greater than 11.0). In this way, an effluent is obtained which can be safely discharged to a fishing stream. An experimental study of this method by the staff of the Water Pollution Research Laboratory showed that simple cyanides (e.g., potassium cyanide) as well as the complex cyanides of zinc, copper and cadmium present in plating wastes were almost completely destroyed by chlorination. The process, however, does not work well with the more stable nickelocyanides.
and these should therefore be excluded since they react only slowly and require a large excess of chlorine. It was also shown that lachrymatory vapours of volatile, extremely toxic cyanogen chloride (CNCI) were formed as intermediate product if the amount of alkali present was insufficient to maintain a pH value high enough to ensure complete hydrolysis of the cyanogen chloride to the relatively harmless cyanate:

\[
\text{At pH} > 8.5: \quad \text{HCN} + \text{Cl}_2 = \text{CNCI} + \text{HCl}
\]
\[
\text{At pH} > 11.0: \quad \text{CNCI} + 2\text{NaOH} = \text{NaCNO} + \text{NaCl} + \text{H}_2\text{O}
\]

The further oxidation of cyanate to nitrate apparently only occurs at pH values less than 11.0. Chlorination of cyanide wastes is now being practised on a commercial scale in America and in this country and the method is reasonably cheap, easy to control, and efficient. Any heavy metals present will precipitate as hydroxides in the alkaline solution and can be removed by settlement. Before discharge to a stream, the alkaline effluent would have to be neutralized with acid and then dechlorinated with sodium thiosulphate.

Chlorination has sometimes been used for the removal of colour in certain industrial waste waters as chlorine is a very effective bleaching agent. Rudolf and Hanlon found that the effectiveness of chlorine for reducing colour in industrial wastes varied with the pH of the trade waste and the form in which the chlorine was applied. For example, sodium hypochlorite, for the same pH value, reduced the colour of rag cooking liquor waste more effectively than did chlorine water, and both these chlorinating agents gave better results at pH 8.0 than at pH 1.3. With some wastes (e.g. rag cooking liquor, and gum wastes) there was, after chlorination, a return of some colour within 10 days.

Ozone, which can be produced commercially by the action of the silent electric discharge on air or oxygen and has found limited use as a sterilizing agent for drinking water, has been proposed as a means of oxidizing cyanide wastes and of destroying phenols in coke oven wastes.

Those interested in the possibility of using chemical oxidation methods for the treatment of trade wastes should consult the valuable paper on the subject by Taylor.

Reduction

Chromium in the trivalent form (i.e. as a chromic salt) is often removed from waste waters by precipitation with alkaline reagents, such as lime. If, however, chromium is present in the hexavalent form (e.g. as a chromate) it cannot be precipitated by alkalis until it is first subjected to the process of reduction so as to convert it to...
the chromic condition. Reduction can be brought about by means of such reducing agents as ferrous sulphate ("copperas"), sulphur dioxide, or sodium metabisulphite \((\text{Na}_2\text{S}_2\text{O}_3)\)\(^{104,105}\), typical equations for the reactions being as follows\(^{104}\):

\[
\begin{align*}
\text{Na}_2\text{Cr}_2\text{O}_7 + 6\text{FeSO}_4 + 7\text{H}_2\text{SO}_4 & = \text{Cr}_2(\text{SO}_4)_3 + 3\text{Fe}_2(\text{SO}_4)_3 + 7\text{H}_2\text{O} + \text{Na}_2\text{SO}_4 \\
\text{Na}_2\text{Cr}_2\text{O}_7 + 3\text{SO}_2 + \text{H}_2\text{O} & = \text{Cr}_2(\text{OH})_3(\text{SO}_4)_2 + \text{Na}_2\text{SO}_4 \\
\text{Na}_2\text{S}_2\text{O}_3 + \text{H}_2\text{O} & = 2\text{NaHSO}_3 \\
\text{Na}_2\text{Cr}_2\text{O}_7 + 3\text{NaHSO}_3 + 5\text{H}_2\text{SO}_4 & = \text{Cr}_2(\text{SO}_4)_3 + 5\text{NaHSO}_4 + 4\text{H}_2\text{O}
\end{align*}
\]

It will be seen that when sulphur dioxide is used, no sulphuric acid is required for the reaction. Thus, although copperas is cheap, the pH must be reduced to a value below 3·0 and preferably as low as 2·0 with sulphuric acid for satisfactory reduction whereas, using sulphur dioxide, reduction takes place effectively within the pH range 1·5–5. Another disadvantage of copperas is the production of large amounts of ferric sulphate, which, when lime is subsequently added to precipitate hydroxides, considerably increases the amount of sludge deposited in the settling tanks; this sludge contains ferric hydroxide in addition to chromic hydroxide and it is not easy to recover chromic oxide economically from such a mixture.

**Simple displacement**

In this type of reaction, one element is replaced by another as when iron reacts with copper sulphate to give ferrous sulphate and copper:

\[
\text{CuSO}_4 + \text{Fe} = \text{FeSO}_4 + \text{Cu}
\]

A practical example of this is the treatment of copper or brass pickle liquors (which contain copper sulphate) with scrap iron or steel in the form of chips, turnings or wire\(^1\); this can be carried out in horizontal flow tanks containing the scrap metal, a period of contact of about 3 hours being allowed. The copper is deposited as a sludge which has a considerable market value. The ferrous sulphate formed can be discharged to a sewer or can be precipitated with lime.

**Double decomposition**

Double decomposition, a chemical reaction involving the mutual interchange of groups, is one of the most widely used chemical methods for the treatment of trade wastes. Strictly speaking, neutralization (page 504), which has been considered separately, comes under this heading.
The commonest reactions involving double decomposition are those in which solutions of metallic salts are treated with alkalis as in the precipitation of copper salts with milk of lime:

\[ \text{CuSO}_4 + \text{Ca(OH)}_2 = \text{Cu(OH)}_2 + \text{CaSO}_4 \]

A widely used application of reactions of this type is the formation of insoluble gelatinous flocs of iron or aluminium hydroxides by the action of iron or aluminium salts on trade wastes; lime or other alkali being also added if insufficient bicarbonate alkalinity is present. These flocs assist in carrying down colloidal and other impurities by adsorption on to the insoluble hydroxide precipitate as explained in connection with the chemical treatment of sewage by this procedure (see page 428) so that after adequate settlement a clear effluent is obtained. The method is often referred to under the names chemical precipitation, chemical coagulation, or chemical flocculation, but the latter name seems to be fashionable today. It affords a valuable means of clarifying wastes containing organic and inorganic colloids as well as finely-divided suspended matter which does not settle easily. The colour in some (though not all) dyehouse waste waters can sometimes be completely removed or very much reduced by coagulation with aluminium sulphate, probably owing to the formation of insoluble aluminium lakes. Flocculation in all these cases is assisted by gentle mechanical stirring with paddles or by means of compressed air.

Harwood has discussed the types of plant used and the applications and limitations of aluminium sulphate in the chemical coagulation of a variety of trade wastes. Among the wastes giving good results are paper mill wastes, sand washery effluents and other waste waters containing colloidal clay, textile wastes, laundry wastes, oil-water emulsions and wastes from power stations containing pulverized fuel ash. It is often most convenient to operate the chemical coagulation plant on the batch or 'fill and draw' system, it is then easier to get a liquid of uniform composition and the dosage of chemical can be more easily controlled. For very large volumes a continuous flow treatment plant may be necessary.

In England, a comparatively cheap commercial form of aluminium sulphate containing a small proportion of ferric sulphate ('alumino-ferric') is much used for the coagulation of trade wastes. The optimum pH value for successful flocculation generally lies in the region not far removed from neutrality (pH usually between 6.0 and 8.4). In cases where aluminium sulphate alone does not give satisfactory results it may be desirable to control the pH by addition of another chemical such as sulphuric acid, lime, sodium aluminate, or sodium carbonate. The optimum dosage of aluminium sulphate must be determined by experiment and may range
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from as little as 20 p.p.m. to 600 p.p.m. or more, depending on the type of waste and its composition. The efficiency of treatment can be assessed by the extent of the reduction achieved in the content of suspended solids and in the 4 hours permanganate value.

Typical results of the action of 'alumino-ferric' on various types of industrial wastes are shown in Table 93 which is adapted from that given in a paper by Harwood106.

Table 93. Results of action of aluminium sulphate ('alumino-ferric') on various types of waste. (After Harwood106)

<table>
<thead>
<tr>
<th>Type of waste water</th>
<th>Treatment</th>
<th>Other chemical (added first)</th>
<th>pH</th>
<th>4 h permanganate value p.p.m.</th>
<th>Suspended solids p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paper mill</td>
<td>40</td>
<td>Na aluminate (30 p.p.m.)</td>
<td>6-5</td>
<td>144</td>
<td>200</td>
</tr>
<tr>
<td>Sand washing</td>
<td>120</td>
<td>Sulphuric acid (900 p.p.m.)</td>
<td>10-5</td>
<td>748</td>
<td>7,300</td>
</tr>
<tr>
<td>Tannery</td>
<td>300</td>
<td>Sulphuric acid (600 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Dyehouse</td>
<td>160</td>
<td>Sulphuric acid (600 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Dyehouse</td>
<td>200</td>
<td>Sulphuric acid (600 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Laundry</td>
<td>400</td>
<td>Sulphuric acid (1,600 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Wood scouring</td>
<td>900</td>
<td>Sulphuric acid (1,000 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Mercerizing</td>
<td>160</td>
<td>Sulphuric acid (1,600 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Pulverized fuel ash.</td>
<td>100</td>
<td>Sulphuric acid (1,500 p.p.m.)</td>
<td>11-0</td>
<td>116</td>
<td>520</td>
</tr>
<tr>
<td>Mine effluent</td>
<td>150</td>
<td>Lime (30 p.p.m.)</td>
<td>6-7</td>
<td>35,000</td>
<td>35,000</td>
</tr>
</tbody>
</table>

Ferrous sulphate ('copperas'), used in conjunction with lime so that the treated liquor is slightly alkaline to phenolphthalein (final pH value 8-4-9-0), is sometimes used for the clarification of industrial wastes but generally does not give such good results as aluminium sulphate. One advantage of copperas over aluminium sulphate, however, lies in the fact that if sulphides are present they are removed as insoluble ferrous sulphide. When carrying out coagulation of wastes with copperas and lime, it is necessary to aerate the mixture so as to oxidize all the precipitated ferrous hydroxide to ferric hydroxide.

Since the early years of the present century, water has been softened
by a newer method rivalling the older lime-soda process, namely
by the so-called ‘base-exchange’ process involving the use of natural
and synthetic zeolites (metal aluminosilicates)\textsuperscript{107-110} which soften
water without producing sludge. The investigations of \textsc{Adams} and
\textsc{Holmes}\textsuperscript{111} in 1935 showed that synthetic resins possessed exchange
properties similar to those exhibited by the zeolites. Resins pre-
pared by condensing phenols with formaldehyde had base-exchange
powers whilst those obtained by the condensation of aromatic
amines (e.g. m-phenylene diamine) with formaldehyde possessed
acid-exchange properties. Thus, by the consecutive use of phenolic
resins and amino resins, it was possible to bring about the complete
removal of dissolved salts from a water. Since these investigations,
other workers have prepared many new and improved ion-exchange
resins. These resins contain, according to \textsc{Topp} and \textsc{Pepper}\textsuperscript{112} “a
cross-linked, high-polymer structure to which are attached ionisable
groups”. It is convenient to regard them as insoluble acids or
bases. Although these newer ion-exchange resins are being used
for the demineralization of water, it is only comparatively
recently that they are finding application in the treatment of trade
wastes.

\begin{table}
\centering
\begin{tabular}{|c|c|c|c|}
\hline
\textbf{pH} & \textbf{Final effluent} & \textbf{p.p.m.} & \textbf{Reduction in 4 h} \textbf{Suspended solids} & \textbf{Reduction in suspended} \textbf{value} & \textbf{per cent} & \textbf{solids per cent} \\
\hline
\textbf{p.p.m.} & \textbf{per cent} & \textbf{value} & & & \\
\hline
6.9 & Nil & 8 & 109 & 96 \\
6.8 & 162 & 24 & 78 & 94 \\
7.2 & 366 & 190 & 16 & over 90 \\
6.0 & 97 & 32 & 16 & 90 \\
6.1 & 79 & 8 & 29 & 97 \\
6.5 & 92 & 46 & 52 & 96 \\
8.4 & 31 & Nil & 28 & 100 \\
6.6 & Nil & -- & -- & 100 \\
6.9 & -- & 20 & -- & nearly 100 \\
\hline
\end{tabular}
\caption{cont.}
\end{table}
Ion-exchange materials are usually divided into the following categories:

(a) **Cation-exchangers** or base-exchangers. These have cation-exchange properties owing to the presence of such groups as $\text{-SO}_2\text{H}$ (strongly acid), $\text{-COOH}$ (weakly acid), or $\text{-OH}$ (very weakly acid). The ions removed from solution are cations or metallic ions such as calcium, magnesium, copper, etc.

(b) **Anion-exchangers** or acid-exchangers. These have anion-exchange properties owing to the presence of such groups as $\text{-NH}_2$ (weakly basic), or the more strongly basic quaternary ammonium group. The ions removed from solution are anions or acidic ions such as $\text{SO}_4^{2-}$, $\text{Cl}^-$ and silicate ions.

The newer cation-exchangers are mainly organic materials which may be sulphonated coal (obtained by the action of fuming sulphuric acid on coal), synthetic resins of the phenolic type or polystyrene type containing an exchangeable hydrogen ion. Synthetic resins have the advantage over the older base-exchange materials (the zeolites) of being resistant to acids. The removal of cations can be represented by the following typical equation, the cation being replaced by hydrogen:

$$\text{CaSO}_4 + 2\text{R} \cdot \text{SO}_2\text{H} = \text{Ca(}\text{SO}_4\text{R})_2 + \text{H}_2\text{SO}_4$$

Effluents from cation exchangers have very low B. coli counts, probably on account of the sterilizing action of the acid formed. Cation-exchange resins can be regenerated by means of excess of dilute acid (e.g. sulphuric acid) which reverses the ion-exchange process:

$$\text{Ca(}\text{SO}_4\text{R})_2 + \text{H}_2\text{SO}_4 = 2\text{R} \cdot \text{SO}_2\text{H} + \text{CaSO}_4$$

When cation-exchange resins are used for softening water, excess of sodium chloride (common salt) is usually used for regeneration:

$$\text{Ca(}\text{SO}_4\text{R})_2 + 2\text{NaCl} = 2\text{NaSO}_4\text{R} + \text{CaCl}_2$$

For a discussion of the characteristics and behaviour of various types of cation exchanger used to soften water the reader is referred to a paper by Streicher and Bowers.

Anion-exchangers, which generally consist of resinous condensation products of formaldehyde with amines and contain amino groups or substituted amino groups (e.g. $\text{-NH}_3$, $\text{-OH}$, or $\equiv\text{N} \ldots \text{OH}$), are used to remove acidic ions from solution. The
removal of anions can be represented by the following typical equation:

\[
\text{HCl} + \text{R-NH}_3 = \text{R-NH}_3 + \text{H}_2\text{O}
\]

Anion-exchangers can easily be regenerated by treatment with such alkaline reagents as ammonia, sodium carbonate and sodium hydroxide.

Complete de-ionization of water for use in certain manufacturing processes can be achieved by passage of the water first through a bed of a cation-exchanger to remove cations and then through a bed of a weakly basic anion-exchanger to remove the anions of mineral acids (e.g. Cl₄, SO₄²⁻, etc.). Any carbon dioxide in solution or as bicarbonate can be eliminated by means of a degasifier. Silica, if present, may require removal by the use of a strongly basic anion-exchanger (see page 102). In this way, a water is obtained almost free from dissolved salts and similar in composition to the best distilled water.

The most useful applications of ion-exchangers in the treatment of trade wastes involve the removal and recovery of metallic constituents (e.g. copper and chromate) from dilute solutions. In general, the method is unsuitable or uneconomic unless some commercially valuable material can be recovered and unless the spent regenerant solution can easily be disposed of.

Table 94, adapted from a paper by MINDLER, gives typical examples of metals which can be removed from certain industrial waste waters by the use of ion-exchange methods.

<table>
<thead>
<tr>
<th>Table 94. Recovery of metals in industrial wastes by ion-exchange methods. (After MINDLER)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cation exchange</strong></td>
</tr>
<tr>
<td>Acid solutions</td>
</tr>
<tr>
<td>Neutral solutions</td>
</tr>
<tr>
<td>Alkaline solutions</td>
</tr>
</tbody>
</table>

The recovery of chromic acid from anodizing baths and rinse waters at the Grumman Aircraft Engineering Corporation, U.S.A.,
is discussed at some length by Mindler\textsuperscript{4} and by Armstrong\textsuperscript{116}. The rinse waters containing chromic acid are passed through a bed of Permutit S (a basic quaternary ammonium anion-exchange resin) which exchanges —OH ions for chromate (CrO\textsubscript{4}\textsuperscript{2—}) ions. Regeneration of the resin with caustic soda gives sodium chromate which is then passed through a cation-exchanger to yield chromic acid. According to Armstrong\textsuperscript{116}, the costs of this method compare favourably with those of a disposal method involving reduction with baulphite.

Experiments on the use of ion-exchange methods for reducing the radioactivity of laboratory waste waters to a safe level have been reported by Ayres\textsuperscript{117}. He showed that the use of cation- and anion-exchangers in series or combined in a single column gave a high decontamination factor,\textsuperscript{*} but a simple cation-exchange unit was sufficient to remove the more harmful radioactive isotopes (e.g. barium, strontium, zirconium, and rare earths) and produce an effluent fit for discharge to the sewers. When the resins become exhausted, they can be incinerated and the radioactive ash disposed of by burial or in containers at sea.

\textbf{Biological Methods}

Although aerobic biological processes (percolating filters, and activated sludge) have been widely and successfully used for many years in industrial areas for the treatment at a local authority's sewage disposal works of trade wastes in admixture with large volumes of domestic sewage, only limited application has hitherto been made of such methods at a trader's premises to industrial waste waters alone. Nevertheless, a noticeable trend, especially in the U.S.A. but also to some extent in this country, is the increasing use within the past few years of biological processes for the treatment and purification of trade wastes despite the many difficulties associated with such methods. Biological filters are very costly to construct and they occupy a great deal of space which may not be easily available on the factory site. The treatment plants would require even more efficient supervision, maintenance, and technical control when dealing with strong industrial wastes fluctuating in composition and volume than would be necessary for the treatment of sewage at a sewage disposal works using biological methods. Hence, an important consideration in the biological treatment of trade wastes is the careful balancing of the wastes as regards strength, volume and pH. Moreover, whilst sewage does contain the right types of

\begin{tabular}{llll}
\hline
No. of disintegrations per minute per ml. of influent & No. of disintegrations per minute per ml. of effluent
\hline
\end{tabular}

\textsuperscript{*} Decontamination factor: \frac{\text{No. of disintegrations per minute per ml. of influent}}{\text{No. of disintegrations per minute per ml. of effluent}}
micro-organisms needed for biological purification this is not necessarily the case with the majority of trade wastes, which may be sterile and may even require the development of specific organisms to be certain of successful results. Some trade wastes may not be amenable to biological treatment on a large scale because they are far too strong, or because of lack of sufficient nutrient materials (especially nitrogen and phosphorus) for the support of micro-organisms, or on account of the presence of toxic substances inimical to bacterial life. It has been shown, however, that bacteria can become acclimatized to a particular poison and an interesting example of this has been reported by Pettet and Mills of the Water Pollution Research Laboratory in connection with waste waters containing cyanides. Their experiments showed that cyanides of potassium, zinc, and cadmium in concentrations equivalent to at least 100 p.p.m. of HCN (i.e. considerably higher than the generally accepted figure of 1-2 p.p.m. of HCN) can be completely broken down to ammonia and oxidized nitrogen in percolating filters without addition of sewage if the filters are gradually acclimatized to cyanide. The destruction of cyanide in copper and nickel cyanides, however, is less complete. Recent work has shown that the organism responsible for the breakdown of cyanides belongs to the group of Actinomycetes (or 'ray-fungi') which represent a kind of transitional stage between bacteria and true fungi.

One of the earliest examples of the successful treatment of trade wastes by aerobic biological methods is afforded by dairy waste waters, which resemble sewage in containing nitrogenous organic matter but are far stronger and undergo putrefaction more easily than sewage. At the time the Royal Commission on Sewage Disposal made its report on the treatment of trade wastes (1915), there was no large scale plant in this country treating dairy wastes satisfactorily by biological methods. As a result of the outstanding investigations carried out by the Water Pollution Research Laboratory during the years 1935-8, the position has undergone a remarkable change and there are now several plants producing final effluents satisfying Royal Commission standards (i.e. B.O.D. not exceeding 20 p.p.m. and suspended solids not more than 30 p.p.m.). Ordinary biological filtration does not work well with dairy wastes because the filters soon become choked with solid matter (fatty material, and masses of fungal filaments). It was found, however, that ponding of the filters did not occur when alternating double filtration (see page 436) was used. With a settled waste of B.O.D. about 200–300 p.p.m. (achieved by dilution, if necessary, with final effluent) and treated by alternating double filtration at a dosage rate of 160 gal./yd.3 of medium per day,
final effluents well within Royal Commission standards were obtained. Investigation of the activated sludge process showed that it gave less satisfactory results owing to its greater sensitivity to flushes of strong liquors and to difficulties associated with the rising and bulking of the sludge.

In the U.S.A., much experimental work has been done on the high-rate biological filtration of industrial wastes and there are many instances of pilot plants and of large-scale plants treating trade wastes successfully by means of biological filters or the activated sludge process. It should, however, be pointed out that since American rivers afford a very much greater dilution, in general, than do their British counterparts, a high degree of purification is usually neither the target nor the achievement. Among some of the industrial wastes treated in the U.S.A. in pilot plants or full-scale plants by high-rate filtration or by activated sludge are milk wastes, coke-oven wastes, de-inking wastes, compressed yeast wastes, brewery wastes, synthetic resin wastes containing formaldehyde, slaughterhouse (or packinghouse) wastes, and cotton finishing wastes.

Biological methods have been proposed for reducing the radioactivity of waste waters. Laboratory experiments by Ruchhöft and Setter, however, on the removal of radioactivity by means of activated sludge indicated that the method was suitable only for wastes with a low level of radioactivity and that certain soluble isotopes (e.g. iodine-131) were only very incompletely removed.

The following are outstanding recent examples in this country of the treatment of trade wastes by aerobic biological methods.

**Cannery wastes**

Dickinson has described the results of operation and the performance of a recirculating plant for the biological filtration of fruit and vegetable cannery wastes. A small degree of nitrification was achieved and the final effluent was generally bright, sparkling and nearly saturated with dissolved oxygen and was usually within the Royal Commission B.O.D. standard for sewage effluents (i.e. B.O.D. less than 20 p.p.m.).

**Viskose-rayon wastes**

Hughes has described the treatment of waste sulphide liquors from a viscose-rayon plant by recirculation on percolating filters handling 50-60 gal. of raw liquor per cubic yard of medium per day. The sulphide liquors are alkaline (200 p.p.m. of caustic soda), have a sulphide content equivalent to about 40 p.p.m. of H₂S, and have a 4 hours permanganate value of 200-250 p.p.m. Metallurgical coke was found to be the most suitable medium for the
ABATEMENT OF POLLUTION II

filters. Apparently, sulphur bacteria develop on the filters, provided the alkalinity is not unduly excessive, and remove sulphide by oxidizing it to sulphate and thiosulphate. The final effluent usually has a pH value of 8.0-9.0, a 4 hours permanganate value of 30-60 p.p.m. and a sulphide content of only about 1 p.p.m. (expressed as $\text{H}_2\text{S}$).

Formaldehyde wastes
A paper of unusual interest by Waldmeier gives the results of operation of an activated sludge plant treating wastes containing formaldehyde and methyl alcohol produced at a factory manufacturing synthetic resin adhesives. The crude wastes could not be dealt with by biological filtration on account of their 'gluey' nature and consequent tendency to cause blocking up of the filter medium. The results showed that a diffused air activated sludge plant gave over 70 per cent purification as judged by the 4 hours permanganate figures. The effluent from this plant was further purified by biological filtration and then mixed with clean condenser water before discharge to the river. The dilution available in the river was low but no harmful effects were observed on the large rainbow trout and smaller brown trout which were 'swimming happily' below the outfall. Although no special nutrients were added to the wastes before treatment, some domestic sewage was present from the factory and from an estate of 50 houses, and the urea-formaldehyde resins probably supplied further amounts of nitrogen.

Chemical wastes
Wilson has given an interesting account of the plant at Ruabon (Wales) for dealing with the chemical wastes of Monsanto Chemicals Ltd. At this plant, very large volumes of waste waters containing phenols, amino-compounds and other organic chemicals are neutralized, settled in clarifiers, and treated by recirculation on high-rate biological filters at a volume loading of about 550 gal./yd. of medium per day. The organisms capable of utilizing these wastes were originally derived from the use of river water. The nutrients (nitrogen and phosphorus) required for the support of biological life appear to be present in sufficient quantity in the wastes. In this way, an almost opaque, greyish-black, unpleasant-smelling liquor is converted to a fairly clear, slightly brownish, odourless liquid, which represents a most notable achievement for which the firm and their staff deserve great credit. Although considerable purification is thus attained, the final effluent does not conform to Royal

* B.O.D. results were valueless with these antiseptic wastes.
† The minimum amount of sewage needed to maintain a healthy activated sludge was about 5 per cent.
Commission sewage effluent standards, but fortunately the effluent receives very ample dilution in a ‘cut’ before discharging to the River Dee, which is famous for its salmon. In view of a recent injunction against the firm as a result of common law action by riparian owners, steps are in progress for further improving the effluent.

Bactericidal chemical wastes

Another example of the biological treatment of chemical wastes in this country has been reported recently by Sharp and Lambden. In this case, the wastes were obtained from the manufacture of various pesticides and insecticides, and were so strongly bactericidal that they had to receive pre-treatment (by adsorption on activated carbon at a low pH value, precipitation of copper with lime, followed by neutralization) before being treated in admixture with settled sewage and river water in percolating filters.

Factors affecting the treatment of industrial wastes by aerobic biological methods have been admirably discussed by Heukelkian who has stressed the fundamental importance of the food available for the micro-organisms (i.e. the chemical composition, the physical state of sub-division, the concentration, the strength, and the carbon:nitrogen ratio of the wastes), the number and types of organisms (i.e. the nature and origin of the ‘seed’ used), and such environmental factors as pH, temperature, oxygen supply and toxic substances. From some further studies by Heukelkian and Gellman, it would appear to be necessary that wastes treated by aerobic biological methods should be neutralized to give a pH value between 6·0 and 8·0 and that nitrogen should be added in readily available form so as to give a B.O.D. to nitrogen ratio of approximately 20:1. Phosphorus is also an essential nutrient for the micro-organisms about 1 part being required for every 75-100 parts of B.O.D. Toxic wastes (e.g. those containing phenols) require seeding, and a considerable time may be needed for the organisms to become acclimatized but by the use of properly adapted seed this lag period can be much reduced. Wastes deficient in nitrogen and phosphorus can be treated in admixture with sewage but if insufficient sewage is available, supplementary additions of nutrients must be added in accordance with the ratios already given. Thus, Helmers and his co-workers, in laboratory studies on the treatment of three nutritionally deficient wastes (cotton kiering waste, rope pulping waste, and brewery waste) with activated sludge, found that these wastes could be successfully treated with as little as 5 per cent by volume of domestic sewage if extra nitrogen (as ammonium sulphate) and phosphorus (as potassium dihydrogen phosphate) were supplied.

Many industrial wastes having a high B.O.D. might prove costly
and difficult to deal with by aerobic biological methods. Work in the U.S.A. has indicated that in such cases treatment by anaerobic digestion can be an efficient means of obtaining large B.O.D. reductions at a relatively low cost. The gas produced by digestion usually contains about 60–70 per cent of methane and is of economic importance as a fuel of high calorific value. Gehr and Morgan have pointed out that wastes to be treated by anaerobic digestion should preferably have the following characteristics:

(i) B.O.D. greater than 500 p.p.m.,
(ii) nitrogen: carbon ratio of at least 1:20,
(iii) high buffer capacity to deal with volatile acids formed by decomposition of organic substances,
(iv) relative freedom from settleable suspended solids,
(v) varied and easily decomposable organic matter,
(vi) reasonably low sulphur content,
(vii) pH value around the neutral point, and
(viii) freedom from toxic substances interfering with biological action.

Laboratory studies and in some cases pilot plant experiments have shown that a variety of difficult wastes characterized by the presence of large amounts of organic matter in solution can be treated by anaerobic digestion. The position has been well summarized by Gehr and Behn, and Table 95 showing the results of the anaerobic digestion of various wastes is taken in part from their paper. It will be seen from this table that the reductions in B.O.D. achieved by anaerobic digestion are very satisfactory, often reaching 80–90 per cent. Nevertheless, the digester effluents still have a very high B.O.D. and consequently are not fit to discharge to the comparatively small rivers of Britain without some form of further treatment (e.g. biological filtration). According to Stander several large scale plants are now using anaerobic digestion for the treatment of certain types of waste (e.g. distillery waste and yeast wastes) and the method gives promise of becoming a useful one for many strong carbonaceous wastes. A limitation is that the waste must have an organic matter content of 1 per cent or more otherwise the process is not an economic one.

A recent novel development in the treatment of certain strong non-toxic wastes containing much soluble organic matter (e.g. penicillin and streptomycin waste waters) has been described by Heukelekian; it involves aeration of the wastes with non-floculent growths consisting of a suspension of finely dispersed cells developed by aerating a soil suspension in the waste liquor. A difference from the activated sludge process is that there is no settlement of the active growths. Activated sludge itself cannot be
used to deal with such wastes because it either disperses or bulks. The addition of nutrients may be necessary if the wastes are deficient in nitrogen and phosphorus. Although effluents from this process have a higher turbidity than the crude wastes, B.O.D. removals of 70–90 per cent are obtained after aeration for 24 hours. Heukelkian has suggested a possible use of this process as a method of pre-treatment before the conventional aerobic biological processes. So far as the author is aware, the method has not yet been applied on a large scale. RUDOLFS and AMBERG have shown in laboratory experiments that 'white water' or 'backwater' from the paper

Table 55. Results of anaerobic digestion of various wastes

<table>
<thead>
<tr>
<th>Type of waste</th>
<th>Loading (lbs. of B.O.D. added to digester per it.3 per day)</th>
<th>Detention period (Days)</th>
<th>5-day B.O.D. of waste after digestion (20° C)</th>
<th>Approx. reduction by digestion per cent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Before Digestion p.p.m.</td>
<td>After Digestion p.p.m.</td>
</tr>
<tr>
<td>Penicillin</td>
<td>0.038</td>
<td>20</td>
<td>6,680</td>
<td>1,270</td>
</tr>
<tr>
<td>Distillery</td>
<td>0.070</td>
<td>—</td>
<td>15,500</td>
<td>1,750</td>
</tr>
<tr>
<td>Compressed yeast</td>
<td>0.100</td>
<td>2</td>
<td>8,000</td>
<td>400</td>
</tr>
<tr>
<td>Wool scouring</td>
<td>0.022</td>
<td>20</td>
<td>1,233</td>
<td>200</td>
</tr>
<tr>
<td>Sealed strawboard</td>
<td>about 0.06</td>
<td>3.1</td>
<td>1,790</td>
<td>605</td>
</tr>
<tr>
<td>Cotton kier</td>
<td>0.014</td>
<td>10</td>
<td>2,660</td>
<td>900</td>
</tr>
<tr>
<td>Meat packing plant</td>
<td>0.084</td>
<td>1.55</td>
<td>2,075</td>
<td>119</td>
</tr>
</tbody>
</table>

machines at paper mills is amenable to treatment by aeration with non-floculent growths at 30° C if nutrient salts are added; the process is also feasible at 50° C—a temperature at which many board mills discharge waste waters. The use of impounding lagoons for the disposal and oxidation of industrial waste waters has very limited application in this country as the treatment does not produce an effluent fit to discharge safely to a small stream. The method has, however, been used to some extent in the wider spaces of America, especially with wastes produced by such seasonal industries as the canning of vegetables and fruit. Anaerobic decomposition of cannery wastes is apt to produce very objectionable odours and to obviate this difficulty to a large extent the addition of sodium nitrate in quantity sufficient to satisfy 20–40 per cent of the 5-day B.O.D. has been recommended. Sodium nitrate helps to maintain aerobic conditions by supplying oxygen and stimulating the growth of green
ABATEMENT OF POLLUTION II

organisms, it also raises the pH and, by maintaining an alkaline reaction, prevents development of acid conditions. The lagoons should be about 3 ft. deep and large enough to store the wastes for 6 months or longer. The wastes must be screened and settled and, according to Rynas148, the B.O.D. should not be greater than 3,600 p.p.m. on account of the risk of odour nuisance and the high cost of the sodium nitrate required. Templeton152 has reported the successful use of open lagoons for the anaerobic digestion at ordinary temperatures of cannery wastes seeded with digested sewage sludge.

Table 95—cont.

<table>
<thead>
<tr>
<th>Gas yield (ft. 3 per lb. of B.O.D. removed)</th>
<th>Temp. °C</th>
<th>pH</th>
<th>Remarks</th>
<th>References (see end of chapter)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7-5</td>
<td>30</td>
<td>7.0</td>
<td>Pilot plant studies</td>
<td>139, 142</td>
</tr>
<tr>
<td>8-0</td>
<td>32</td>
<td>7.2</td>
<td>Pilot plant</td>
<td>139, 143</td>
</tr>
<tr>
<td>14</td>
<td>30</td>
<td>7.2</td>
<td>Pilot plant</td>
<td>139, 143</td>
</tr>
<tr>
<td>8-5</td>
<td>30</td>
<td>7.2</td>
<td>Pilot plant</td>
<td>139, 143</td>
</tr>
<tr>
<td>9-1</td>
<td>34</td>
<td>7.2</td>
<td>Pilot plant (Oct. 1950–March 1951)</td>
<td>144</td>
</tr>
</tbody>
</table>

SOME DIFFICULT TRADE EFFLUENT PROBLEMS

GAS LIQUOR21, 153, 153A

When bituminous coal with a fairly high volatile matter content is distilled in retorts at a gas works and the volatile products are condensed, it yields in addition to coke and gas a distillate which separates into two layers, viz. a lower dark brown tarry layer (used for the manufacture of organic chemicals, drugs, dyes, etc.) and an upper aqueous layer known as ammoniacal gas liquor which raises a difficult disposal problem153B. The amount of this liquor produced per ton of coal carbonized averages about 32-52 gals., the quantity depending on the type of retort used, the moisture content of the coal and other factors21. Ammoniacal gas liquor contains much ammonia (free, and also combined as chloride, carbonate, etc.), pyridine and other organic bases, phenols (monohydric
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and polyhydric), small amounts of cyanide, sulphide, and thiocyanate (see analysis in Appendix, page 588) and traces of pyrene and other polynuclear hydrocarbons. It is one of the most difficult wastes to purify satisfactorily and very serious pollution results if it is discharged untreated to a stream. The polluting effects of gas liquor on a stream are due chiefly to the following factors:

(a) The very high oxygen demand of the liquor. The 4 hours permanganate value may be as high as 12,000 p.p.m., i.e. the liquor would be about 120 times as strong as an average domestic sewage.

(b) The presence of such constituents as cyanides, phenols and ammonia which are toxic to fish and other river life, and inhibit bacterial action.

(c) The presence of phenols can give rise to complaints of tastes and odours if the water is to be used as a source of domestic supply. The tastes and odours are especially pronounced and reminiscent of ‘T.C.P.’ if the water is chlorinated, owing to the formation of chlorinated phenols (see Chapter 3, page 52).

When distillation is carried out in coke ovens for the production of metallurgical coke using bituminous coal of rather lower volatile matter content than that used at a gas works, the liquor produced, although similar in general character to gas works liquor, is much weaker but usually has a considerably higher cyanide content.

When ammoniacal gas liquor is distilled in a current of steam in a so-called ‘ammonia concentrator plant’, ammonia, hydrogen sulphide, and hydrogen cyanide are evolved. The ‘spent gas liquor’ from the still is somewhat weaker than the original ammoniacal liquor, having a much lower ammonia content and containing very little sulphide and cyanide (see Appendix, page 588). The amount of spent liquor produced may easily amount to more than 100 gal./ton of coal carbonized.

The customary method of disposal of gas liquor is, as already pointed out earlier in this chapter (page 494), to discharge it to the public sewers. The amount of spent gas liquor that can be dealt with satisfactorily at a sewage works using biological methods of purification is generally not more than 0.5 per cent of the sewage flow, whilst in the case of the much stronger crude ammoniacal liquor (free from tar), this figure should not exceed 0.25 per cent (cf. page 494). The nationalization of the gas industry in this country has involved the closing down of many of the smaller gas works and the setting up of much larger units as a result of which the sewage works may be far too small to cope with the increased volume of gas liquor produced. In such cases, the disposal of the liquor raises most difficult problems. Limited quantities of the liquor can
be dealt with by application as a fertilizer to land (page 486). Research is in progress on the biochemical oxidation of the liquor in percolating filters and by activated sludge. Chemical methods of oxidation are also being studied, a process using nitric acid on a pilot-plant scale being of particular interest. But the most promising solution of the problem is the so-called 'Tingley' process first proposed by Nicklin and used at the gas works at Tingley, Yorkshire; it aims at the complete treatment of the liquor (with recovery of such by-products as phenols and ammonium chloride) so as to give a final effluent fit to discharge to a stream. This scheme for the treatment of crude ammoniacal gas liquor consists of the following stages:

(i) Extraction of the ammoniacal liquor with 'benzole' (commercial benzene) to remove monohydric phenols.
(ii) Steam distillation to remove much free ammonia and hydrogen sulphide.
(iii) Evaporation of the resulting spent liquor under reduced pressure in a Scott evaporation plant to about 10 per cent of its original volume.
(iv) Extraction of the higher phenols with butyl acetate.
(v) Further evaporation of the liquor to recover ammonium chloride.
(vi) The effluent (distillate from evaporators) is finally passed through activated carbon filters to remove the remaining phenols so that it can then be used for coke quenching or else discharged to a stream.

The extent of the purification achieved in these various stages can be gauged by the following figures, quoted by Egan, obtained in a trial run:

<table>
<thead>
<tr>
<th>Stage</th>
<th>Permanganate value (p.p.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crude ammoniacal liquor</td>
<td>13,800</td>
</tr>
<tr>
<td>Dephenolated liquor</td>
<td>9,560</td>
</tr>
<tr>
<td>Ammonia concentrator plant</td>
<td></td>
</tr>
<tr>
<td>Scott distillate from evaporators</td>
<td>4,920</td>
</tr>
<tr>
<td>effluent liquor</td>
<td></td>
</tr>
<tr>
<td>Final effluent from carbon filters</td>
<td>50</td>
</tr>
</tbody>
</table>

The percentage purification attained, based on the permanganate figures for the crude liquor and final effluent, works out at over 99.6 per cent—certainly a very remarkable achievement.
Several difficulties in connection with the operation of the Tingley plant have been experienced, notably

(i) formation of much gummy material in the evaporators caused blockages in the system and rendered the butyl acetate plant unworkable,

(ii) the activated carbon filters had to be renewed more often than was originally anticipated, and

(iii) the recovered ammonium chloride darkened on exposure to air, thus reducing its market value.

Some of these difficulties have been overcome (e.g. the higher phenols are now destroyed by a chemical oxidation process instead of being recovered), but the very high, almost prohibitive, cost of the process (of the order of £2 per 1,000 gal. of liquor treated) is a disturbing feature and seems likely to restrict the use of the process only to those cases where treatment at a sewage works or on land is not feasible. However, a modified form of 'Tingley' plant is being constructed by the North Western Gas Board at Denton, near Manchester, and the results of the operation of this plant will be awaited with great interest.

Much can often be done at the gas works to reduce the strength of the gas liquor by making certain process alterations or modifications, e.g. use of electrostatic precipitators to remove tar from the hot gas, and reduction of thiocyanate formation by admitting air to the stream of gas as late as possible.

**KIER LIQUORS**

Kier liquors ('black liquors') are obtained by the digestion of cotton, rags, esparto grass, straw and other similar materials containing cellulose with a solution of caustic soda under pressure in iron vessels called 'kiers'.* This treatment removes dirt and resinous and fatty material, thereby setting free the true vegetable fibre, cellulose, which is then repeatedly washed with water until free from alkali. The liquors so obtained are dark brown in colour, very strongly alkaline (pH 12·0 or over), and contain a very high concentration of polluting organic matter. (See Appendix, Tables 121, 122.)

Perhaps the worst of all these liquors is obtained in the digestion of straw for paper making. When discharged to a river, this liquor not only causes pollution (see Appendix, Tables 118, 119 for effect on River Irwell) but also produces an objectionable appearance with much scum and froth on the surface of the stream especially below

* The boiling in alkaline solution of cotton yarn and piece goods is also called 'kiering'; the liquors are of a similar nature to the above kier liquors but are generally much weaker.
weirs where aeration occurs. A good illustration of the persistence of this froth is shown by the case of a sample of straw kier liquor from a paper mill, which, when subjected to a frothing test by shaking in a half-filled Winchester quart bottle for 1 minute gave a froth 2 in. in height which was still 1 in. high after standing overnight! Depending on the method used, the volume of ‘black liquor’ obtained from each ton of straw can vary between 500 and 1,000 gal., and in addition many thousands of gallons of dilute wash waters are produced, the first washings being particularly strong. Since a big firm might easily process 1,000 tons or more of straw per week, it is easy to see that the volume of grossly polluting liquors can be very great. Unfortunately, straw processing increased greatly in this country during and after World War II on account of the shortage of esparto grass and wood pulp.

Kier liquors are difficult to treat satisfactorily by means of chemical coagulants. PORGES and his associates using cotton kier liquor have shown that very high doses of chemicals are required and large quantities of voluminous sludge that are difficult to settle are produced. Moreover, much of the organic matter is in true solution and cannot be precipitated. Partial purification of kier liquors can be effected by acidifying with sulphuric acid which precipitates part of the organic matter and removes some colour; the sludge produced by this method settles only with great difficulty and the resulting liquor is still of a very polluting character. Although the best method of disposal is to discharge the kier liquor to the sewers for treatment in admixture with sewage, this is often impracticable (even if the liquors are neutralized) on account of the high organic load they would put on the biological units, unless the sewage works is a very large one capable of providing great dilution of the wastes. If disposal to a sewage works is not feasible, or if no sewer is available, the only method of proved reliability of dealing with kier liquor is to evaporate and incinerate the liquor for the recovery of caustic soda in a special ‘caustic soda recovery plant’ (see page 499). Being constructed of steel, these plants are very expensive (they may cost up to about £200,000). Moreover, only crude liquor and first washings can be dealt with since it would be uneconomic to evaporate large volumes of weak wash waters. The washing of straw is more difficult than was the case when esparto grass was used in pre-war days as raw material, hence the very large volumes of wash waters produced from straw. Thus, whilst 85 per cent of the caustic soda could be recovered from the liquors when esparto grass was used, only about 55 per cent can be obtained from straw kier liquor in the soda recovery plant. The problem

* Some saving in expensive acid can be achieved by the use of the cheaper carbon dioxide (flue gases) for partial neutralization.
of the disposal of the more dilute kier wash waters has not yet been satisfactorily solved. Experiments carried out at the Water Pollution Research Laboratory \(^{59}\) have shown that the liquors would need neutralization with carbon dioxide, addition of nutrients, and preliminary dilution with water to bring the B.O.D. down to about 150-200 p.p.m. before treatment in percolating filters. The large volumes of water or sewage necessary for dilution purposes might not always be available on a large scale. Anaerobic digestion has been used on a pilot plant scale for the treatment of cotton kier liquor (see Table 95, page 520) but although the process can deal with undiluted liquor, the effluents are still of a polluting character and would require biological filtration to render them fit to discharge to a stream in this country. NEMEROV \(^{160}\) has claimed that an aeration procedure carried out on neutralized cotton kier liquor removed up to 77 per cent of the B.O.D., but the treated waste, judged by British standards, was still of a polluting character with a B.O.D. of over 500 p.p.m.

**SULPHIDE DYE LIQUORS**

As a rule, waste waters from the dyeing of cotton goods are not as polluting today, when synthetic dyes are mostly used, as they were in former times when natural wood and vegetable dyes were popular. A notable exception, however, is provided by the very noxious and polluting wastes produced in so-called 'sulphide dyeing'. The dyes used in this method ('sulphur dyes' or 'sulphide dyes') are prepared by fusing organic nitrogen compounds with sulphur and alkali. They are used to produce fast blacks, browns, dark blues and dark greens on cotton. The dyes are relatively cheap and their fastness to light, washing and acids makes them specially useful for dyeing textiles for the Services (e.g. khaki materials). Since the dyes are insoluble in water, they are dissolved in a solution of sodium sulphide and the reduced solution thus obtained is applied near the boiling point, the cotton being kept below the surface for 30-60 minutes. The dye-bath may contain dyestuff in quantity equal to 1-20 per cent of the weight of the material, sodium sulphide (at least equal in amount to that of the dyestuff), sodium carbonate and salt.\(^{161}\) The dyed material is then exposed to air, to oxidize the reduced dyestuff fully, and washed with soap. The spent dye liquors produced from this process are very foul, being opaque, highly coloured, strongly alkaline as a rule, and high in sulphide content. PORGES and his co-workers\(^{162}\) quote the case of a waste containing much sulphide which had a deep blue-black colour, a pH value of about 11-7, and a B.O.D. of about 20,000 p.p.m. It is usually difficult to treat these liquors so as to produce an
effluent suitable for discharge to a river, but treatment with ferrous sulphate (copperas), or the use of sodium hypochlorite or bleaching powder to destroy the sulphide, can usually be relied upon to give an effluent fit to pass to the sewers.

With spent dye liquors that are not too alkaline, treatment with copperas followed by addition of lime to pH about 8.5, preferably using air-blowing, gives good clarification and colour removal as a rule and sulphide is precipitated as insoluble ferrous sulphide. The amounts of copperas required for flocculating sulphide dye wastes can, however, be very large if the liquors are strong. Thus, Barracough found it necessary to use as much as 10,000–20,000 p.p.m. of copperas. Experience has shown that very strongly alkaline sulphide dye wastes do not respond easily to chemical precipitation and the sulphide often has a tendency to come down in a black colloidal form instead of in a flocculent settleable condition. When attempts are made on a large scale to reduce the high alkalinity of such wastes by treatment with acid before addition of copperas and lime, it is difficult to avoid odour nuisance due to local excesses of acid causing liberation of foul-smelling hydrogen sulphide—one can, indeed, sympathize with workmen who go on strike for as good a reason as this!

TANNERY WASTES

Tanning is the process of conversion of the skins of animals into the tough non-putrescible material known as 'leather'. The processes used in tanning skins are complex and varied, giving rise to the intermittent discharge of a variety of grossly polluting waste waters.

Vegetable tanning, used mainly for heavy leathers (e.g. belts and soles of footwear) is carried out with extracts of oak bark, quebracho, sumach and other vegetable materials rich in tannins. Chrome tanning finds application for the preparation of the lighter leathers, such as kid gloves and the uppers of shoes, and involves treatment with chromium salts obtained by the reduction of sodium dichromate in sulphuric acid solution with glucose or other suitable reducing agent. Chamois leather is usually prepared by an oil tanning process. Synthetic tanning agents are also used today in the preparation of various types of leather. Whichever process of tanning is employed, certain preliminary treatment of the skins is necessary to clean them and remove the hair. The more important processes used in tanneries, then, involve

(a) soaking the skins in water to remove dirt, blood, preservatives used in curing, and other filth,
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(b) treatment with lime ("liming") and sodium sulphide to soften and remove the hairs,

c) de-lining with dilute acids and "bating" with enzyme preparations,

d) tanning, and

e) various finishing processes, including dyeing and coating, which, however, only provide a negligible proportion of the total wastes.

Broadly speaking, therefore, there are two main types of waste water produced at tanneries, namely:

(i) Liquors resulting from the soaking, liming and de-liming of the skins ("beam-house wastes"). These are alkaline, grossly polluting liquids containing organic matter, hair, lime, sulphide, and a high proportion of ammoniacal nitrogen and organic nitrogen.

(ii) Somewhat acidic highly coloured spent tannin liquors ("tann- yard wastes") whose composition depends upon the method of tanning employed. Vegetable tanning wastes contain more polluting organic matter than do chrome tanning wastes but the latter are more difficult to treat by biological processes on account of the presence of inhibitory chromium compounds.

The methods used for dealing with tannery wastes give, in general, only partial purification and the resulting effluents cannot be discharged to a small river without causing much pollution. For instance, mixing the alkaline and acidic effluents precipitates much sludge which can be removed by settlement in tanks but, although there is a considerable reduction in B.O.D., the final effluent is still alkaline and of a polluting character. Such processes as chemical coagulation and biological filtration also only bring about partial purification.

A troublesome problem in the disposal of tannery wastes is the presence of large amounts of sulphide in the spent liming wastes. The use of copperas for the removal of sulphide causes difficulties by producing ferrous sulphide in a black colloidal state and also by yielding large quantities of sludge which create an awkward disposal problem. Chlorination to destroy sulphide has been tried but owing to the high chlorine demand is very expensive. A method effective for removing sulphide from sulphide wastes produced in the manufacture of viscose rayon, namely treatment on percolating filters to oxidize sulphide by means of sulphur bacteria (page 516), would seem to be ruled out so far as tannery wastes are concerned on account of their excessive alkalinity and the presence of large amounts of organic matter.
Wherever possible, tannery wastes should be dealt with, after adequate pre-treatment (e.g. screening to remove hairs, and removal of settleable solids), by discharge to the local sewers followed by biological treatment in admixture with sewage at a sewage works of sufficient capacity.  

In conclusion, it must be emphasized that there is much scope for further research on the development of improved methods for the treatment of tannery wastes and this is best carried out at the tannery itself as it may well involve considerable changes in the processes used in tanning (for instance, replacement of sodium sulphide by some other suitable but less polluting substance).  

Radioactive Waste Waters  

The production of radioactive waste waters in considerable volumes arises from the recent development of nuclear reactors and atomic energy stations and the use of radioactive isotopes for medical, industrial and research purposes (cf. Chapter 3, pages 47-51). The volumes are likely to show big increases when atomic power stations are set up in the future.  

Methods for the removal of radioactivity from wastes have been mentioned under the appropriate treatment process in this chapter (cf. pages 498, 500, 514, 516), and, in general, are similar to processes used for the treatment of other types of trade waste. Although the methods are not in reality difficult to carry out, nevertheless, in view of the ever present health hazard and the possibility of contaminating drinking water supplies, elaborate precautions have to be taken to ensure that the processes used are adequate and fool-proof.  

The particular methods employed depend upon the nature of the radioactive isotopes present. Evaporation and storage suffice for the short-lived isotopes. Such processes as ion-exchange, chemical precipitation or coagulation and biological treatment, can be used to transfer most of the radioactivity from large volumes of solution to comparatively small volumes of sludge or solid material, which can then be disposed of at sea or by burial in porous soil. Liquid wastes of low activity can be discharged to sewers, an estuary or even to an inland river, but all discharges in this country are subjected to careful control, being assayed for radioactivity by the radiochemical inspector of the Ministry of Housing and Local Government.  

A detailed discussion of the methods for the disposal of radioactive wastes is beyond the scope of this book and for further details the reader is referred to the chapter on radioactive wastes by C. P. Straub in Rudolf's book on Industrial Wastes and to a paper by
KENNY dealing with the problem of the disposal of radioactive wastes in Britain.

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CHAPTER 14
STANDARDS FOR RIVERS, SEWAGE EFFLUENTS AND TRADE EFFLUENTS

I often say that if you can measure that of which you speak and can express it by a number, you know something of your subject; but if you cannot measure it, your knowledge is meagre and unsatisfactory.

LODGE KELVIN

GENERAL CONSIDERATIONS

Those who for many years have advocated the setting up of standards of purity for sewage effluents and trade effluents discharging to our inland streams received overwhelming support for their views in the 1949 Ministry of Health Report whose general recommendations were subsequently implemented in the Rivers (Prevention of Pollution) Act, 1951. An important feature of the 1949 Report was the recommendation that powers should be given to river boards to make by-laws fixing standards for effluents discharging to streams* and that standards should be prescribed in relation to tests for measuring the general properties of a polluting effluent. In a circular issued by the Ministry of Housing and Local Government, the following tests were suggested by an expert committee as a basis for fixing standards:

Well-established tests suitable for adoption now:

(i) Suspended solids.

(ii) B.O.D. (5 days, 20°C).

(iii) pH value.

(iv) Temperature (°C).

Certain further tests under consideration:

(v) Organic carbon, or, 4 hours permanganate value.

(vi) Fish toxicity test.

(vii) Colour.

(viii) Test for repression of natural self-purification processes.

(ix) Test for liquids immiscible in water.

In three of these cases (fish toxicity, colour and repression of natural

* In Section 5 of the 1951 Act, it is left open whether effluent standards, stream standards, or both, should be prescribed.
self-purification), the committee stated that no suitable test is in existence or could be suggested. Tests for specific constituents are regarded as impracticable since all the possibilities could never be included. It is, nevertheless, admitted that such tests might prove simple and useful in certain cases. In the writer's opinion, trade effluents can vary so much in composition and can contain such a variety of substances that the imposition of standards based on a limited number of tests is unlikely to be adequate. It is also noteworthy that no tests for turbidity (or transparency), radioactivity, froth, dissolved solids, sulphides, or soluble iron are included although pollution can be caused by any of these. For example, excessive dissolved solids (such as sodium chloride) might be harmful to water weeds and fish food as well as to fish. Sulphide is not only toxic to fish but also objectionable on account of its unpleasant odour, its tendency to blacken lead paint and copper articles and its liability to lower the redox potential of the river. A standard for iron in solution (ferrous and ferric) is also desirable since, in contact with the natural bicarbonate alkalinity of river water, iron yields precipitates of insoluble iron hydroxide (cf. Chapter 3, page 35) and so can be regarded as potential suspended matter.

Some river boards have adopted "working standards" for effluents which are published in their annual reports. These standards are useful for the guidance of local authorities and manufacturers but have no legal force. There are, however, two ways open to a river board of providing legally recognized standards under the 1951 Act, viz. (i) by making by-laws in accordance with Section 5 of the Act, or (ii) by means of a Section 7 consent (cf. Chapter 2). Before making by-laws, a river board must carry out a thorough survey of the river or rivers for which standards are required. Data needed for this purpose would have to include flow measurements and analyses of the stream at a number of points and information on the volumes and character of all sewage effluents and trade effluents discharging to the stream. A decision would have to be made on the quality of water needed in the river, or in different parts of the same river and, in this connection much would depend, to use the words in Section 5 of the Act, on 'the extent to which the stream is or may in the future be used for industrial purposes, fisheries, water supply, agriculture, transport or navigation'. By-laws must be confirmed by the Minister of Housing and Local Government in order to have any legal standing. Some disadvantages of by-laws are well summarized in an annual report of the Bristol Avon River Board:

"Attractive as by-law standards might appear to those industrialists who want to know what degree of purification their effluents are expected to meet, the writer believes that standards are not legally enforceable and are, therefore, of little practical use. It is considered that any satisfactory system of sewage and trade effluent control must necessarily be based on a thorough study of the hydrography and ecology of the river and of the sewage and trade effluents to which it is subjected."

"The committee stated that no suitable test is in existence or could be suggested. Tests for specific constituents are regarded as impracticable since all the possibilities could never be included. It is, nevertheless, admitted that such tests might prove simple and useful in certain cases. In the writer's opinion, trade effluents can vary so much in composition and can contain such a variety of substances that the imposition of standards based on a limited number of tests is unlikely to be adequate. It is also noteworthy that no tests for turbidity (or transparency), radioactivity, froth, dissolved solids, sulphides, or soluble iron are included although pollution can be caused by any of these. For example, excessive dissolved solids (such as sodium chloride) might be harmful to water weeds and fish food as well as to fish. Sulphide is not only toxic to fish but also objectionable on account of its unpleasant odour, its tendency to blacken lead paint and copper articles and its liability to lower the redox potential of the river. A standard for iron in solution (ferrous and ferric) is also desirable since, in contact with the natural bicarbonate alkalinity of river water, iron yields precipitates of insoluble iron hydroxide (cf. Chapter 3, page 35) and so can be regarded as potential suspended matter."
to reach, the difficulty of reconciling every possible type of waste with all kinds of flow conditions and various water uses suggests that by-law control may prove so rigid as either to impose undue hardship on those discharging effluents or give rise to very real risks in water utilization. Unlike its Scottish equivalent, the English Act of 1951 does not permit a river board to allow a lower standard than that prescribed by by-laws.

By-laws fixed by a river board do not necessarily represent the last word on the subject as it is still possible for a riparian owner to take proceedings against a manufacturer or a local authority under common law (cf. Chapter 2, page 15) and in this way require the discharge to meet a much stricter standard than that demanded by a river board. It is interesting to note that the Rivers (Prevention of Pollution) Bill, as originally drafted, took away the common law rights of riparian owners when a standard had been established by a river board, but, owing to much opposition from all sides, when the matter was before the Standing Committee of the House of Commons, this provision was withdrawn and the common law rights were restored in what eventually became the Rivers (Prevention of Pollution) Act, 1951.

The issue of a Section 7 consent by a river board to manufacturers or local authorities can only be done where there are new discharges, or existing discharges which have altered substantially in volume, composition, temperature or rate of discharge. Within the next 20 years or so, however, it is probable that many existing effluents will have increased in volume or character to such an extent as to constitute an altered discharge which can be dealt with under Section 7 of the Act.

A river board can, even in the absence of any legal standards, prosecute a firm or a local authority under Section 2 of the 1951 Act if it can be proved that matter which is "poisonous, noxious or polluting" is being discharged to a stream, but in this case until October 1958 (i.e. seven years after the passing of the Act) the consent of the Ministry is first required. For the sake of preserving good relations, such a course would only be pursued by a river board as a very last resource, for instance in the event of persistent refusal to take reasonable steps to stop the pollution.

There has been some diversity of opinion on the relative merits of effluent standards and stream standards as devices for protecting the stream from pollution. In the U.S.A., stream standards rather than effluent standards are preferred for legal purposes and this is understandable in a country where, in general, rivers are large and pollutions occur at wide intervals. In this country, stream standards serve a useful purpose mainly as a basis for classifying rivers.
ASPECTS OF RIVER POLLUTION

In concluding these general observations, it can be stated that any standards put forward by a river board ought to satisfy the following requirements:

(i) The standards must be capable of precise definition.
(ii) Reliable methods of analysis must be available for determining whether the effluent or test sample infringes the standards.
(iii) The standards should be neither too lenient nor too stringent since in the former case some pollution of the river may occur and in the latter case unnecessary expenditure may be incurred by the trader or the local authority.
(iv) The standards should be practicable, that is possible to attain by reasonable means.

STANDARDS FOR RIVER WATERS

The Royal Commission on Sewage Disposal in the course of investigations on the quality of the water of a number of rivers in this country suggested a classification of river waters into groups (very clean, clean, fairly clean, doubtful and bad) based on the general visible condition of a stream as indicated by such characteristics as smell, degree of turbidity, presence or absence of fish, presence of suspended matter, nature of algal growth, etc. The observed physical and biological condition of the stream was correlated with the average analytical figures of the water above and below a sewage outfall and the results, taken from the Royal Commission Reports 4, 5 are given in Tables 96 and 97.

Table 96. Average analytical figures for river waters above and below sewage outfall:

<table>
<thead>
<tr>
<th>Observed condition</th>
<th>Susp. solids</th>
<th>Chlordode, mll.</th>
<th>Oxygen in solution when analysed</th>
</tr>
</thead>
<tbody>
<tr>
<td>River water</td>
<td>p.p.m.</td>
<td>p.p.m.</td>
<td>p.p.m.</td>
</tr>
<tr>
<td>Very clean</td>
<td>0.5</td>
<td>15</td>
<td>7.8</td>
</tr>
<tr>
<td>Clean</td>
<td>0.25</td>
<td>15</td>
<td>7.8</td>
</tr>
<tr>
<td>Fairly clean</td>
<td>0.35</td>
<td>15</td>
<td>7.8</td>
</tr>
<tr>
<td>Doubtful</td>
<td>0.6</td>
<td>15</td>
<td>7.8</td>
</tr>
<tr>
<td>Bad</td>
<td>10</td>
<td>15</td>
<td>7.8</td>
</tr>
</tbody>
</table>

* Usually referred to as Royal Commission river classification.

The B.O.D. test was regarded by the Royal Commission as the most reliable chemical index of quality of a river water as regards

* An additional group between 'fairly clean' and 'doubtful', namely 'moderately clean', was later dropped since the B.O.D. of this group was found to be almost identical with the B.O.D. of the 'fairly clean' group.
STANDARDS FOR RIVERS AND EFFLUENTS

organic content and, accordingly, the B.O.D. figures in Table 96 considered in relation to the observed physical and biological condition of the stream have since been known as the 'Royal Commission river classification'. In connection with the use of this classification, it should be borne in mind that it is not safe to place undue reliance upon the B.O.D. figure obtained from a single sample.

Table 97. Classification of rivers in accordance with their visible degree of cleanliness, based on riverside observations under normal summer conditions. (From 8th Report of Royal Commission on Sewage Disposal)

<table>
<thead>
<tr>
<th>Condition of river water</th>
<th>Very clean</th>
<th>Clean</th>
<th>Fairly clean</th>
<th>Doubtful</th>
<th>Bad</th>
</tr>
</thead>
<tbody>
<tr>
<td>Suspended matter</td>
<td>Clear</td>
<td>Clear</td>
<td>Fairly clear</td>
<td>Nightly turbid</td>
<td>Turbid</td>
</tr>
<tr>
<td>Opalescence</td>
<td>Bright</td>
<td>Bright</td>
<td>Slightly opalescent</td>
<td>Opalescent</td>
<td>Opalescent</td>
</tr>
<tr>
<td>Smell on shaking in bottle</td>
<td>Odourless</td>
<td>Faint carthy smell</td>
<td>Putrid</td>
<td>Smelly</td>
<td>Soap, fetid or putrid</td>
</tr>
<tr>
<td>Appearance in bulk</td>
<td>Clear</td>
<td>Clear</td>
<td>Slightly brown and opalescent</td>
<td>Black</td>
<td>Brown or black and soapy looking</td>
</tr>
<tr>
<td>Delicate fish</td>
<td>May be plentiful</td>
<td>Present</td>
<td>Probably absent</td>
<td>Absent</td>
<td>Absent</td>
</tr>
<tr>
<td>Coarse fish</td>
<td>Clean and bare</td>
<td>Clean</td>
<td>Plentiful</td>
<td>Absent</td>
<td>Coated with brown growth and deposit</td>
</tr>
<tr>
<td>Stones in shallows</td>
<td>Clean and bare</td>
<td>Covered with fine light brown deposit</td>
<td>Plentiful</td>
<td>Coated with brown or black mud</td>
<td>Scarcely</td>
</tr>
<tr>
<td>Stones in pools</td>
<td>Scarcely</td>
<td>Plentiful</td>
<td>Lightly coated with brown fluffy deposit</td>
<td>Plentiful</td>
<td>Plentiful and covered with fluffy deposits</td>
</tr>
<tr>
<td>Water weeds</td>
<td>Scarcely</td>
<td>Plentiful</td>
<td>Lightly coated with brown fluffy deposit</td>
<td>Plentiful</td>
<td>Plentiful and covered with fluffy deposits</td>
</tr>
<tr>
<td>Green algae</td>
<td>Scarcely</td>
<td>Plentiful</td>
<td>Plentiful and covered with fluffy deposits</td>
<td>Present</td>
<td>Abundant in green algae</td>
</tr>
<tr>
<td>Grey algae, Insects, larvae, etc.</td>
<td>Scarcely</td>
<td>Moderate quantities in shallows</td>
<td>Present</td>
<td>Abundant in green algae</td>
<td></td>
</tr>
</tbody>
</table>

The other figures given in Table 96 might almost equally well serve as a basis of stream classification. Indeed, the Trent River
Board prefers a river classification based on the 4 hours permanganate value rather than on B.O.D., doubtless because the prevalence of metallic contamination in the streams around Birmingham (a great centre of the metal industries) makes the B.O.D. test unreliable as an index of organic pollution. A classification of rivers given in an annual report of the Trent River Board and based upon the 4 hours permanganate value, the prominent animal life present, and upon the use to which the river is put is shown in Table 98.

Table 98. Classification of rivers by Trent River Board according to prominent animals present, 4 hours permanganate value, and use

<table>
<thead>
<tr>
<th>Class of stream</th>
<th>Prominent animals present</th>
<th>Approximate permanganate value p.p.m.</th>
<th>Suggested 'use' classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Trout, grayling, caddis and may-flies</td>
<td>0-3</td>
<td>Domestic water supply</td>
</tr>
<tr>
<td>B</td>
<td>Chub, dace, water shrimps and snails</td>
<td>3-6</td>
<td>Watering cattle; some manufacturing processes and wash waters</td>
</tr>
<tr>
<td>C</td>
<td>Roach, gudgeon, hop-lace (Asellus) and leeches</td>
<td>6-10</td>
<td>Industrial cooling; unsafe for cattle</td>
</tr>
<tr>
<td>D</td>
<td>No fish, bloodworms (red chironomids)</td>
<td>10-20</td>
<td>Industrial cooling only after treatment; unsuitable for amenity use</td>
</tr>
<tr>
<td>E</td>
<td>Barren, or with fungus and small worms (Tubifex)</td>
<td>Over 20</td>
<td>Navigation and emergency use only; possible danger to public health</td>
</tr>
</tbody>
</table>

The Royal Commission on Sewage Disposal worked out a number of 'limiting figures' for river waters falling between the 'fairly clean' and 'doubtful' classes and these are set out in Table 99.

Table 99. Royal Commission on Sewage Disposal. 'Limiting figures' for river waters

<table>
<thead>
<tr>
<th>Test</th>
<th>'Limiting figure', which, if exceeded, would probably result in nuisance p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-day B.O.D. (18-3°C)</td>
<td>4</td>
</tr>
<tr>
<td>4 hours x/80 permanganate value</td>
<td>4</td>
</tr>
<tr>
<td>Alkali-soluble nitrogen</td>
<td>0-45</td>
</tr>
<tr>
<td>Suspended solids</td>
<td>15</td>
</tr>
<tr>
<td>Dissolved oxygen when drawn</td>
<td>4 ml/1 (3-7 p.p.m.)*</td>
</tr>
</tbody>
</table>

* About 60 per cent of saturation at maximum summer temperature (18-3°C).
The Royal Commission took the view that a river giving the limiting figures shown in Table 99 would be on the verge of causing nuisance (e.g. bad smells), and in the event of these figures being exceeded, the river would be liable to show signs of pollution except in unusually cold weather. Of the figures given in this table, the critical B.O.D. figure of 4 p.p.m. is very important as it forms the basis of the normal B.O.D. standard recommended by the Royal Commission for sewage effluents discharging to inland rivers (see 'Standards for sewage effluents', pages 547-58).

The recommendations of the Royal Commission regarding the oxygen balance of polluted streams can, then, be summarized as follows:

(a) B.O.D. (5 days, 18-3°C) of river water must not exceed 4 p.p.m. 4, 5.
(b) Dissolved oxygen content of river water must not fall below 4 ml/l., i.e. about 60 per cent of saturation at 18-3°C or 65°F (the presumed maximum summer temperature) 5, 7.

These two standards are not entirely independent since, according to the Royal Commission, a minimum dissolved oxygen content of 60 per cent of saturation can only be maintained if the B.O.D. of the river water does not exceed 4 p.p.m. Most of the rivers examined by the Royal Commission were, however, slow to sluggish rivers. In this connection, Roberts' has pointed out that the rate of re-aeration of a river water depends upon the physical characteristics of the stream; being very much lower with deep sluggish streams than with rapid shallow streams (cf. also Chapter 6, page 143). It is, therefore, to be expected that the conclusions of the Royal Commission regarding oxygen balance will not necessarily apply to streams of the rapid shallow variety.

Many river boards in this country have, as a working basis, adopted the Royal Commission classification of streams based upon B.O.D. The Mersey River Board has for practical reasons found it desirable to extend the classification by the addition of two extra classes. Within the area covered by this Board there are many polluted industrial rivers some of which only just fall within the 'bad' class whilst others are subject to very gross pollution. In order to indicate more satisfactorily these differences in the degree of organic pollution, samples falling within the 'bad' class are now divided into the three categories of 'poor', 'bad' and 'very bad' in accordance with the scheme set out in Table 100. This classification is intended as a rough guide only and is fairly satisfactory if the pollution is predominantly of an organic nature measurable by the B.O.D. test and so long as toxic substances are not present in sufficient concentration to cause material interference.
with the test. Both these conditions generally hold throughout most of the Board’s rivers. In practice, however, it is found that there are some cases in which the quality of a river water cannot be assessed solely on the basis of B.O.D. and it may then be necessary to adjust the classification after considering all the relevant analytical data. Cases in which this may be desirable include samples containing the following:

1. Acidity to methyl orange (i.e. pH value less than 4.0).
2. Marked alkalinity to phenolphthalein (pH value above about 9.0).
3. High dissolved mineral solids.
4. Toxic substances (e.g. metallic contamination, phenols, cyanides).
5. Oil or other immiscible liquid.
6. An abnormally high or low dissolved oxygen content.
7. Organic matter having a high 4 hours permanganate value.
8. Considerable suspended matter, unless this is ‘natural’ silt, clay or sand derived from the river bed.

Table 100. Royal Commission classification of rivers used by Mersey River Board

<table>
<thead>
<tr>
<th>5-day B.O.D. of river (20°C) p.p.m.</th>
<th>Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 or less</td>
<td>Very clean</td>
</tr>
<tr>
<td>About 2</td>
<td>Clean</td>
</tr>
<tr>
<td>About 3</td>
<td>Fairly clean</td>
</tr>
<tr>
<td>About 5</td>
<td>Doubtful</td>
</tr>
<tr>
<td>About 7-5</td>
<td>Poor</td>
</tr>
<tr>
<td>About 10</td>
<td>Bad</td>
</tr>
<tr>
<td>20 or more</td>
<td>Very bad</td>
</tr>
</tbody>
</table>

Analytical data on some Lancashire river waters of low B.O.D. and containing abnormal constituents necessitating an adjustment of the Royal Commission classification are given in Table 101 (pages 548-9).

A classification of river waters by IMHOFF and FAIR based upon the use to which the water is put is given in Table 102.

Several authorities in the U.S.A. concerned with water pollution control in the Ohio River Basin, the Tennessee Valley, West Virginia, and the Potomac River Basin have suggested standards of water quality for water supplies, fishing, bathing and boating. Readers interested in this subject will find a good review and discussion in papers by STEVENSON and STREETER. The standards vary a little according to the particular authority. For fishing streams,
the recommended pH ranges are usually in the region 6.5-8.6; the daily minimum dissolved oxygen content suggested is 5 p.p.m. with a monthly average, in general, of 5.5-6.5 p.p.m.; and the monthly average B.O.D. should fall within the range 1.5-4.0 p.p.m. No toxic substances, oils, tars, free acid, floating solids, or debris (except from natural sources) should be present.

STANDARDS FOR SEWAGE EFFLUENTS

In connection with the formulation of standards for sewage effluents discharging to rivers, it is obviously of great importance to be able to calculate the effect of a polluting effluent on the composition of the river water.

If we know the relative volumes of an effluent and of the river into which it discharges and the composition of each in terms of B.O.D. or other measured property, then if we assume that there is no volume change on mixing and that the composition of the mixture is intermediate between that of the effluent and river, the following general formula applies:

\[ M(V_E + V_R) = EV_E + RV_R \]

\[ M = \frac{EV_E + RV_R}{V_E + V_R} \]

where

- \( E \) = a measured property (e.g. B.O.D., temperature, etc.) of the effluent
- \( R \) = corresponding measured property of River
- \( M \) = corresponding measured property of Mixture
- \( V_E \) = relative volume of Effluent
- \( V_R \) = relative volume of River

This formula can be used in all calculations involving mixtures of two effluents or of an effluent and river water, and enables any one unknown to be computed if the values of the other magnitudes are known. It must be remembered, however, that it is assumed that complete mixing has taken place, that no volume change occurs on mixing, and that no marked chemical interactions occur—assumptions which are not always strictly true in practice. For example, the B.O.D. of a mixture of a nitrified percolating filter effluent and an un-nitrified activated sludge plant effluent cannot be accurately computed from the formula on account of the occurrence of nitrification (cf. Chapter 10, page 385).

The Royal Commission on Sewage Disposal\(^*\) derived a formula similar to formula (2) when arriving at a B.O.D. standard for a sewage effluent discharging to an inland stream providing dilution with a minimum of 8 volumes of river water.
Table 101. Examples of inland rivers with a low B.O.D. and with classification amended due to presence of abnormal constituents

<table>
<thead>
<tr>
<th>Class</th>
<th>Abnormal constituents</th>
<th>pH</th>
<th>Chloride (p.p.m.)</th>
<th>Transmittance mm. cm. through</th>
<th>KMnO₄ value (p.p.m.)</th>
<th>M.B. stability (° C days)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Caustic alkalinity (lime), suspended matter</td>
<td>10:8</td>
<td>8</td>
<td>500</td>
<td>&gt;600</td>
<td>0*</td>
</tr>
<tr>
<td>B</td>
<td>Copper, suspended matter (flakes)</td>
<td>7:1</td>
<td>6</td>
<td>94</td>
<td>600</td>
<td>14:2</td>
</tr>
<tr>
<td>C</td>
<td>Suspended matter (coal dust)</td>
<td>8:1</td>
<td>58</td>
<td>0</td>
<td>415</td>
<td>18:0</td>
</tr>
<tr>
<td>D</td>
<td>Natural pollution by acid peaty matter after heavy rain</td>
<td>3:6</td>
<td>15</td>
<td>52</td>
<td>65</td>
<td>33:4</td>
</tr>
<tr>
<td>E</td>
<td>Acid mine drainage</td>
<td>5:2</td>
<td>540</td>
<td>236</td>
<td>270</td>
<td>44:0</td>
</tr>
<tr>
<td>F</td>
<td>Chromate, high ammoniacal N</td>
<td>6:0</td>
<td>46</td>
<td>600</td>
<td>&gt;600</td>
<td>3:0</td>
</tr>
<tr>
<td>G</td>
<td>Suspended matter (clay and fine sand) from sand-wastery</td>
<td>7:0</td>
<td>21</td>
<td>27</td>
<td>227</td>
<td>1:4</td>
</tr>
<tr>
<td>H</td>
<td>Salt (sodium chloride)</td>
<td>7:2</td>
<td>27,600</td>
<td>475</td>
<td>555</td>
<td>1:4</td>
</tr>
</tbody>
</table>

* Using 25 per cent phosphoric acid, instead of 25 per cent sulphuric acid, in this test, the figure is 7:6 (Chapter 3, page 277).

Table 102. Standards for river waters according to Limhoff and Fair

<table>
<thead>
<tr>
<th>Class</th>
<th>Use</th>
<th>Standard or standards</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Drinking water, after chlorination</td>
<td>Without filtration, B. coli less than 50 per 100 ml.</td>
</tr>
<tr>
<td>B</td>
<td>Bathing, recreation and shellfish culture</td>
<td>No visible sewage matters, B. coli less than 100 per 100 ml.</td>
</tr>
<tr>
<td>C</td>
<td>Fishing</td>
<td>Dissolved oxygen content not less than 3 p.p.m. and preferably 5 p.p.m. Carbon dioxide not more than 40 p.p.m. and preferably 20 p.p.m. Absence of nuisance, odours, and unsightly suspended floating matters. Some dissolved oxygen present</td>
</tr>
<tr>
<td>D</td>
<td>Rough industrial uses and irrigation</td>
<td></td>
</tr>
</tbody>
</table>

Adopting the symbols used by the Royal Commission, namely

\[ z = \text{dilution} = \frac{\text{proportion of river water to effluent}}{\text{calculated on the basis of the D.W.F. of the river}} \]
\[ x = \text{B.O.D. of effluent (p.p.m.)} \]
\[ y = \text{B.O.D. of river water (just above effluent outfall) in p.p.m.} \]

\[ z = \frac{x}{y} = 8 \]

Then

\[ y = R = 2 \text{ (B.O.D. in p.p.m. of a 'clean' river water)} \]
Taking the figure of 4 p.p.m. (compare this chapter, page 545) as the limiting figure or maximum safe B.O.D. of the mixture, \( M \), of effluent and river water, then substituting in formula (2) we get

\[
4 = \frac{(x \times 1) + (2 \times x)}{1 + 2} \quad \ldots \quad (3)
\]

\[
x + 16 = \frac{x + 20}{9}
\]

Therefore

\[
x = 36 - x + 16
\]

or

\[
x = 20 \text{ p.p.m.}
\]

This means that in order to avoid nuisance (i.e. to give a mixture of river water and effluent not exceeding 4 p.p.m. in B.O.D.) a sewage effluent diluted with 8 times its volume of clean river water (B.O.D. 2 p.p.m.) must comply with a B.O.D. standard of 20 p.p.m. A margin of safety was provided because in the view of the Royal Commission `the great majority of effluents are diluted by more than 8 times their volume of river water`. If the diluting river water is not clean, then of course much larger volumes of diluting water would be needed. For example, suppose the river is only ‘fairly clean’ with a B.O.D. of 3 p.p.m., then the formula shows that instead of 8 volumes of river water, 16 volumes would be required to give a mixture not exceeding 4 p.p.m. in B.O.D.
This limiting standard of 20 p.p.m. B.O.D. constitutes one of the well-known normal standards proposed by the Royal Commission for sewage effluents and, it may be repeated, the fundamental basis of this standard is that the B.O.D. of the mixture of effluent and river water below the effluent outfall must not exceed the critical figure of 4 p.p.m. at 65° F and at the D.W.F. of the river. An additional standard of 30 p.p.m. was also fixed as the upper limit for the content of suspended solids in a sewage effluent, this figure being fairly easily attained in practice and being regarded as sufficiently low to prevent appreciable deposition of sludge.

The two normal standards recommended by the Royal Commission, namely (i) 5-day B.O.D. at 65° F not to exceed 20 p.p.m., and (ii) suspended solids content not to exceed 30 p.p.m., were regarded by the Commission as the general standards for sewage effluents receiving dilution by at least 8 volumes of clean river water and were intended to apply so long as the dilution was not greater than 150 volumes of river water. A series of standards for each dilution between 8 and 150 volumes was rejected as impracticable. With a dilution exceeding 150 volumes but less than 300 volumes the B.O.D. standard was dropped altogether and the suspended solids standard was further relaxed to 60 p.p.m., whilst with dilutions between 300 and 500 volumes the suspended solids standard was further relaxed to 150 p.p.m. No numerical standards were considered necessary when the dilution exceeded 500 volumes but it was suggested that, for the sake of the appearance of the river, removal of grit, heavier particles of suspended matter, faces, paper, etc., should be carried out. Cases in which stricter standards for sewage effluents might be required owing to the very small volume of diluting river water were regarded by the Royal Commission as exceptional and no standards for such cases were defined.

The recommendations of the Commission concerning standards for sewage effluents are summarized in Table 103.

It will be noticed that although the Royal Commission used formula (3) for arriving at a normal B.O.D. standard suitable for the majority of places, they did not suggest the general application of that formula for determining standards in each individual case for this would have involved different standards of purity for every sewage effluent. There would have been difficulties in administration as well as uneven distribution of cost between different authorities in the same watershed; those lower down, where the quality of the stream water was worse, being at a disadvantage compared with those upstream.

It is noteworthy that the majority of sewage effluents falling within the scope of the investigations of the Royal Commission received dilution by more than 8 volumes of river water. Circumstances
have, however, changed considerably since those days and there are today many cases in which the dilution provided is much lower than eightfold and the diluting water is certainly far from ‘clean’. Moreover, since the days of the Royal Commission, there have been increases in population in many areas, the proportion of trade wastes to sewage has increased, the D.W.F. of many streams has fallen, and consequently the proportion of sewage effluent to river water has risen. In one case, within the area of the Mersey River Board\(^1\), the ratio of sewage effluent to river water, at present about 9:1, will within a few years rise to about 27:1 due to an increase in the D.W.F. of the sewage. Here we have the unusual case of an effluent diluting a stream, a state of affairs hardly envisaged by the Royal Commission. It is to be expected, therefore, that changed times and circumstances will require standards for sewage effluents far stricter than those suggested by the Commission, and Table 104 gives examples of sewage disposal works where the final effluent receives little dilution and consequently more stringent standards have been proposed or are actually in use.

### Table 104. Royal Commission on Sewage Disposal\(^\*\). Standards recommended for sewage effluents\(^*\) discharging to inland streams

<table>
<thead>
<tr>
<th>Type of standard</th>
<th>Volumes of clean diluting river water available</th>
<th>Standards p.p.m.</th>
<th>Type of treatment suggested</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Maximum permitted B.O.D.(^1) (5 days, 60° F)</td>
<td>Maximum permitted suspended solids</td>
</tr>
<tr>
<td>Normal</td>
<td>150</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>over 150</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Relaxed</td>
<td>150–300</td>
<td>—</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>300–500</td>
<td>—</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>over 500</td>
<td>—</td>
<td></td>
</tr>
<tr>
<td>Strict</td>
<td>Less than 8</td>
<td>Standards not defined, but to be decided on basis of local circumstances</td>
<td>See Chapter 12, pages 456 ff</td>
</tr>
</tbody>
</table>

* Not applicable to warm-water summers.

\(^1\) This number of days is according to the standard temperature of insulation in the B.O.D. test. It is an average of the time in the B.O.D. of a sample so that the Royal Commission standards are slightly more stringent if based on a 20° C determination.

The case of Luton, which stands at the head of the River Lee, where there is little or no dilution available, is particularly interesting since this borough is now producing what must surely be the
best sewage effluent, derived from an industrial sewage, in this country. Before 1948, however, although Luton Corporation produced a reasonably satisfactory effluent judged by ordinary standards, there was considerable pollution of the River Lee since the dilution by river water was negligible especially during the summer—another case of river water being diluted by effluent. As a result, the Corporation was involved in a common law case in 1948 brought by the riparian owners on that portion of the river (Lord Brocket, Brocket Estates Ltd., and Mr F. M. Gingell). In July, 1948, the Judge granted an injunction restraining Luton Corporation from "causing or permitting any matter or substance (whether liquid or solid) to flow or pass into the River Lee" until the same shall have been properly treated and purified so as not to cause pollution or to be a nuisance or cause of injury to the Plaintiffs. Although no reference was made in the injunction to any particular standards of purity, in practice the problem set to the Corporation was to produce an effluent which, without any dilution, would form a reasonably acceptable river water and this was done by filtering the humus tank effluent through sand filters or micro-strainers (cf. Chapter 12, page 457). During an application in November 1952 for the extension of the period of suspension of the injunction, it was stated by the Plaintiffs that since nitrates (normal constituents
of good sewage effluents) encouraged growth of certain aquatic plants not attractive to trout and suppressed the favourable flora, the Corporation must remove nitrates, but must also ensure that the final effluent was almost free from ammonia—conflicting demands which are virtually impossible of attainment! Another baffling but so far insoluble problem set to Luton Corporation was to discover means for eliminating from the final effluent synthetic detergents and other substances causing foam on the river. It is gratifying, therefore, in concluding this brief account of the Luton case, to report that the parties concerned eventually came to terms for the removal of the injunction and the stay of proceedings, and it was agreed by the riparian owners that Luton Corporation had at great cost done everything reasonably practicable to improve their sewage effluent and so largely diminish the pollution of the river.

It is nearly 50 years since the Royal Commission proposed sewage effluent standards based upon B.O.D. and suspended solids. It is not surprising, therefore, that since those days additional standards for sewage effluents have been suggested. As Lovett has pertinently remarked: 'Would we be satisfied nowadays with public highways, public transport, public cleansing, street lighting, water supply, gas and electricity distribution, etc., as they were 50 years ago?' As an illustration of present-day trends, it is of interest that the Mersey River Board has adopted the following working standards for sewage effluents discharging to coarse-fishing streams as well as industrial rivers:

(i) B.O.D. (5 days, 20°C) shall not exceed 20 p.p.m. (Royal Commission sewage effluent standard).
(ii) Suspended matter shall not exceed 30 p.p.m. (Royal Commission sewage effluent standard).
(iii) Effluent shall pass the methylene blue stability test (5 days, 20°C).
(iv) Effluent shall contain not less than 10 p.p.m. of nitrate (expressed as N).

It will be seen that, besides the two classical Royal Commission standards, additional standards for stability and nitrate are included. The necessity for including a stability test is amply demonstrated by long experience over many years in Lancashire where there have been a number of cases of sewage effluents, particularly from activated sludge plants, conforming to the Royal Commission standards for B.O.D. and suspended solids and yet failing to pass a stability test (see, for example, Chapter 10, page 378). Admittedly there are special conditions obtaining in the Mersey River Board area where the majority of streams consist of sewage effluents and...
trade effluents and there is very little dilution by clean water in dry weather. Under these conditions it is obvious that the stability of an effluent discharging to these rivers is at least as important as the B.O.D. or content of suspended matter, and, where the available dilution is small, may even be the most vital factor, for the ability of a river to maintain aerobic conditions must depend largely upon the stability of the effluents composing it. Indeed, Mr. J. H. Garner, a leading authority on river pollution in this country, stated in his evidence in the common law case Lord Brocket v. Luton Corporation\textsuperscript{18} that, in his opinion, the Stability or Putrescibility test is the most important test that can be applied to a sewage effluent. As already stressed in a previous chapter (see Chapter 10, page 377), the presence of nitrates has a great stabilizing influence on a sewage effluent by delaying the fall in redox potential to the level at which hydrogen sulphide is produced. It is interesting to note that there is now a legal precedent for a stability test since an "incubator test"\textsuperscript{*} has been included, in addition to the two Royal Commission tests, in the Hertfordshire County Council Act of 1937\textsuperscript{21} for the effluent from the sewage disposal works of the Colne Valley Sewerage Board (see Addendum to this chapter).

Much has been written and there has been considerable diversity of opinion about the value or otherwise of nitrates in sewage effluents. This subject has received some discussion in previous chapters (see Chapter 3, pages 55-6 and Chapter 10, pages 377-8) but perhaps a short review and re-statement of the position is appropriate at this stage. There has been much controversy in recent times between exponents of the two rival biological sewage purification processes on the value of nitrates in sewage effluents. In general, the standard low-rate percolating filter gives final effluents having a high content of nitrate (usually of the order 10-50 p.p.m. expressed as N), the amount depending of course on the strength and character of the sewage and other local circumstances. Since short-circuiting can occur in a filter bed it is naturally quite possible for a percolating filter effluent to be unsatisfactory as regards the B.O.D. and yet contain a substantial proportion of nitrate. On the other hand, activated-sludge plants as usually run in this country give a well-clarified effluent satisfactory as regards B.O.D. and content of suspended matter but generally containing about 10 p.p.m. or more of ammoniacal nitrogen and little or no nitrate. Lockett\textsuperscript{22}, however, has shown that at the Mogden works of the Middlesex County Council it is well worth the small extra cost of carrying the purification process to an advanced state of nitrification because a rapid-settling dense activated sludge is thereby obtained which can withstand better any shock loads of

\* Not the methylene blue test, but a test based on a similar principle.
strong sewage or trade waste. These experiences have been confirmed by Griffiths at the works of the Colne Valley Sewerage Board, near Rickmansworth.

The problem has also to be considered in relation to the effect of the final effluents on the receiving stream. Imhoff has shown that in some of the rivers and lakes of Germany sewage effluents containing nitrates, phosphates, and other fertilizing salts, stimulate excessive growths of algae and other water plants during the summer months to such an extent that pollution occurs later on due to death and decay of these plants, thus causing much mortality amongst fish. The fertilizing effect of the nitrates appears to be dependent also on the simultaneous presence of phosphates. In these cases, it seems advisable to reduce the concentration of nitrates and other fertilizing constituents to as low a level as possible and Imhoff suggests this can be done by means of spray irrigation, which requires large areas of land, or by the use of shallow ponds in which algae are allowed to grow and so remove the nitrates and other fertilizing salts.

In many English rivers, in particular in the heavily polluted streams of Lancashire, the West Riding of Yorkshire and the Midlands, conditions are quite different. Thus, the Lancashire rivers are, in general, quite small. They consist mainly of sewage effluents and trade effluents with very little clean water in dry weather and, moreover, the summers are relatively cool and less sunny than in Germany and consequently are much less likely to stimulate excessive algal growths. Indeed, there is little evidence in this country of any marked pollution caused by algae in flowing streams as distinct from lakes and other stagnant waters. In these circumstances, the presence of nitrates in sewage effluents discharging to the rivers of Lancashire is regarded by the river boards as essential because if the dissolved oxygen content of the stream becomes exhausted, on account of heavy organic pollution, the river will have the benefit of a reserve of nitrate to prevent septic action and nuisance by smell. Thus, an activated-sludge plant effluent containing no nitrate and little dissolved oxygen, even if complying with Royal Commission normal standards, might well tend to cause odour nuisance in a small stream in warm weather. Advantages of well-nitrified activated sludge effluents discharging to small fishing streams are:

(a) their ammoniacal nitrogen content will necessarily be low and, since ammonia is toxic even in small amounts to fish (cf. Chapter 7, page 168 and Chapter 10, page 372), there is much less danger of damage to fisheries caused by the presence of ammonia; and

(b) they will tend to stimulate reasonable growth of water plants.
which, provided they are not excessive, are of great value in a
fishing stream in helping to supply extra dissolved oxygen in
hot weather and in providing food for the stream fauna.

An un-nitrified effluent discharging to a fishing stream affording
low dilution is particularly undesirable, not only on account of the
presence of toxic ammonia but also because the oxidation of am ­
monia to nitrate in the stream takes place at the expense of the dis­
solved oxygen of the stream water. According to Southgate, this
nitrification of ammonia in streams may occur at fairly short
distances below the point of entry of an effluent.

Other advantages of the presence of nitrates in rivers have been
stressed by Locke, who referred to the useful part played by
nitrates in helping to oxidize phenols and sulphur compounds in
streams and to laboratory experiments showing that nitrate assists
in the maintenance of conditions suitable for the aerobic rather
than the anaerobic digestion of sludge on the stream bed.

The reader may be reminded here of what was pointed out
previously (Chapter 3, page 55), namely that during the hot sum­
mer months, there are numerous instances of the deliberate addition
of sodium nitrate (a somewhat expensive chemical) to polluted
streams in the U.S.A. in order to prevent the development of
objectionable smells. In this country, we regard it as simpler
and cheaper to benefit our streams by adding nitrate in the form of
sewage effluents.

Roberts has rightly drawn particular attention to the great im­
portance of the presence of dissolved oxygen in sewage effluents
especially when they discharge to a small stream providing low
dilution. In this connection, he writes:

'An effluent of B.O.D. 20 p.p.m. saturated with oxygen has a
similar demand on the oxygen of a stream as one of B.O.D.
11 p.p.m. denuded of oxygen, and the immediate effect of the
lower B.O.D. effluent might well be more harmful. Particularly
is this the case when inadequate dilution of the effluent is
present ...'

It would, however, seem scarcely necessary to have a special
standard for dissolved oxygen in sewage effluents; a well-nitrified
stable effluent will almost invariably contain plenty of dissolved
oxygen.

The sewage of many local authorities in industrial areas contains
a great variety of trade wastes. For instance, even as far back as
1939, no less than 89 different trades produced liquid effluents
passing to the sewers in the Manchester area alone. It is,
therefore, argued by some that standards for effluents from industrial
sewages should include limiting standards for poisonous metals, phenols and other toxic substances likely to be found in trade wastes. Although such limiting standards would have to be included in any by-laws made under Section 5 of the 1951 Act, it would seem to be unnecessary to include such standards in the ordinary working standards of a river board as the discharge of poisonous matter to a stream is definitely prohibited by Section 2 of the 1951 Act. Indeed, the Royal Commission on Sewage Disposal did not consider that properly purified effluents derived from industrial sewages would contain toxic substances in sufficient concentration to cause damage to fish life. In the 5th Report of the Commission the following appears on the subject of chemical poisons in effluents:

'We have not yet studied this point in much detail, but we think that very few effluents in which the organic matter had been well oxidized would contain chemical poisons in quantity sufficient to do harm to fish life, and that the heavy metals would be brought down in the sludge. When Leeds sewage was known to contain a considerable quantity of arsenic, the effluent from its biological filtration showed only minute traces of it.'

In general, this conclusion appears to be true of well-purified effluents from biological treatment plants. Rudolph and Zuber, for example, have shown that toxic metals, such as copper, zinc and chromium, are readily removed from aqueous solutions by fresh sewage solids and by activated sludge due to adsorption on to the organic matter in these materials. Nevertheless, the author is not altogether satisfied that the generalization of the Royal Commission regarding chemical poisons is not subject to some exceptions and further work on the subject seems desirable, especially in the cases of effluents containing detergents and other residual materials discharging to a stream affording a low dilution.

A minor but not inconsiderable advantage of having a nitrate standard is that a fall in nitrate in the final effluent may constitute the first warning that excessive amounts of toxic substances are present in the sewage. In fact, nitrification of a sewage effluent is generally inhibited by small amounts of toxic substances before other indicators of the quality of an effluent (e.g. B.O.D.) are appreciably affected. Thus, Rideour and Greenbank showed that 1·1–1·6 p.p.m. of cyanide (expressed as HCN) interfered with nitrification in the activated sludge process. Similarly, Pettet and Thomas found that 2 p.p.m. of cyanide (expressed as HCN) began to interfere with nitrification of sewage in percolating filters but had little effect on the B.O.D. of the effluent. Again, Hill has shown that small amounts of nickel (1–3 p.p.m.) definitely
inhibit the nitrification of sewage by activated sludge though not significantly affecting the clarification. Edwards and Nussberger\textsuperscript{33} report that the accidental discharge of a large volume of chromate wastes to the Tallmans Island (New York) activated sludge plant had little effect on the treatment of the sewage but caused nitrification to cease for about 10 days. Jenkins and Hewitt\textsuperscript{34} found some deterioration in nitrification in the activated sludge process when the chromate concentration reached about 2 p.p.m. (expressed as Cr) but percolating filters were able to tolerate rather higher amounts of chromate before nitrification was affected adversely. All these results suggest that inhibition of nitrification is the first warning signal that dangerous amounts of toxic substances may be present in sewage.

It must be remembered that sewage effluents conforming to Royal Commission standards are still impure from the bacteriological standpoint and are liable to contain large numbers of bacteria of intestinal origin and possibly also, particularly during epidemics, pathogenic organisms (cf. Chapter 5, pages 59-60, and Chapter 8, pages 246-8). River waters receiving these effluents are not, therefore, safe as sources of drinking water for human consumption unless subjected to proper treatment and sterilization by the waterworks authority.

**STANDARDS FOR TRADE EFFLUENTS**

In the 9th Report of the Royal Commission on Sewage Disposal dealing with trade wastes\textsuperscript{35}, limiting figures of 40-60 p.p.m. of suspended solids were suggested for trade effluents discharging to inland streams—the exact value depending upon the nature of the effluent. Apart from a B.O.D. standard of 40 p.p.m. for a few trade effluents, there was little or no guidance on other standards. The most comprehensive list of 'working' standards for trade effluents discharging to inland streams\textsuperscript{*} is that adopted by the Mersey River Board and is given in Table 105. It must be emphasized that when the effluents discharge to industrial rivers, which is generally the case, the standards cannot always be rigidly applied and some relaxation is permitted if the effluents are being treated by the best practicable means. It is not proposed to consider these standards here in detail as a full discussion has appeared in the literature\textsuperscript{36}, but a few comments of a general nature may not be out of place. It will be noticed that the Mersey River Board, following the precedent set by the Royal Commission, has adopted

\* When trade effluents discharge to the sewers of a local authority, the final effluent from the sewage works is expected to comply with sewage effluent standards.
separate standards for sewage effluents and for trade effluents. There is, of course, no theoretical reason why the same set of standards should not apply equally well to both sewage effluents and industrial effluents. The separation into dual standards has, however, been made on practical grounds, since, in practice, it is found that the known methods of trade effluent purification do not in the majority of cases produce final effluents complying with the Royal Commission sewage effluent B.O.D. standard of 20 p.p.m.

Table 105. Mersey River Board: working standards for trade effluents discharging to inland streams

<table>
<thead>
<tr>
<th>Substance</th>
<th>Standard</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Settled transparency (as mm depth seen through)</td>
<td>Not less than 100 mm</td>
<td></td>
</tr>
<tr>
<td>pH value</td>
<td>Between 5 and 9</td>
<td></td>
</tr>
<tr>
<td>Suspended solids</td>
<td>Not more than 40 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Suspended solids + dissolved metals*</td>
<td>Not more than 60 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>4-hour O.A. from acid KMnO₄ at 27°C</td>
<td>Not more than 50 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Alkalinity to P.P. (as CaCO₃)</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Acidity to M.O. (as CaCO₃)</td>
<td>Not more than 1 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Sulphide (as H₂S)</td>
<td>Not more than 0·2 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Oils and grease</td>
<td>Not more than 10 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Not more than 1 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Phosphates</td>
<td>Not more than 1 p.p.m.</td>
<td></td>
</tr>
<tr>
<td>Free chlorine</td>
<td>None</td>
<td></td>
</tr>
<tr>
<td>Tar</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chromium (expressed as Cr)</td>
<td></td>
<td>Shall not exceed 1·0 p.p.m.</td>
</tr>
<tr>
<td>Arsenic</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silver</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Copper</td>
<td>individually or in total</td>
<td></td>
</tr>
<tr>
<td>Mercury</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cadmium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Barium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Selenium</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lead</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nickel</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Soluble solids</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Insecticides or radioactive material</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Any other substance toxic to fish or fish food</td>
<td>None</td>
<td></td>
</tr>
</tbody>
</table>

* Applies to metals in solution (e.g. iron, aluminium) which could give precipitates with the natural alkalinity of the river water.

There is, therefore, no practical justification for a trade effluent standard that is at present impossible of attainment by practicable and reasonably available means. Moreover, a B.O.D. standard is not always suitable for trade effluents as the test is influenced too much by the presence of toxic substances. The Mersey River Board has, therefore, adopted for trade wastes, containing...
organic pollution, a standard based upon the 4 hours permanganate value, which is set at the somewhat lenient level of 60 p.p.m. simply because in practice it is found that by use of some form of chemical precipitation many trade wastes can reach this standard but would have great difficulty in attaining a much lower figure. However, certain trade wastes free from toxic substances and containing nitrogenous organic matter (e.g. dairy wastes) are expected to conform to the normal Royal Commission sewage effluent standards (i.e. B.O.D. not more than 20 p.p.m., and suspended solids not more than 30 p.p.m.) since such wastes are similar in composition to sewage and are, in general, amenable to biological methods of purification.

It may be noted that the standards are not related to the relative volumes of effluent and river water. On the River Irwell watershed, where there are discharges to the main river (which is only 38 miles long) and its tributaries of nearly 200 trade effluents and nearly 100 sewage effluents, it would scarcely be practicable to have some 300 sets of standards!

It will be observed that no standard for colour is prescribed. Under the 1951 Act, a river board in making by-laws may prescribe a standard "for the purpose of determining when matter is to be treated as poisonous, noxious or polluting by reason of its effect in discoloring a stream". The difficulties involved in framing a standard—whether a by-law standard or a working standard for limiting the colour of a discharge have already been mentioned previously (see Chapter 3, page 36). It would seem that before such a standard can be put forward with any confidence much more work will have to be done on the nature, properties and effects of substances causing colour in different types of effluent.

In by-laws and in Section 7 consents made under the Rivers (Prevention of Pollution) Act, 1951, a river board can specify a standard for temperature. In general, it is best to impose an upper limit to the temperature of the effluent discharging to the stream. In some cases, however, it may be desirable to place a limit on the temperature of the stream at a specified point below the discharge, or on the temperature rise at the point of entry of the discharge or other specified point. A difficulty with a standard based upon stream temperature rather than effluent temperature is that the temperature of a stream can vary according to the depth since heated effluents tend to float over the top of the cooler stream water. An advantage of stipulating a standard based on effluent temperature is that such a temperature is easy to measure by a river inspector and by the firm or authority concerned, and consequently there is no difficulty in knowing when the standard is being infringed. An effluent temperature standard is necessary in
cases where samples discharge into inaccessible culverts or into 'dry' watercourses.

As examples of working standards for effluents discharging to fishing streams, we can consider those put forward by the Severn River Board\textsuperscript{37}, which are given in Table 106. Being designed for the protection of fishing streams, these standards are naturally somewhat stricter than those of the Mersey River Board which serves a predominantly industrial area. The Severn River Board do not normally ask for stricter standards than those shown in Table 106 unless unsatisfactory stream conditions arise.

Table 106. Working standards applied to effluents discharging to rivers in Severn River Board area\textsuperscript{37}

<table>
<thead>
<tr>
<th>Substance</th>
<th>Standard</th>
</tr>
</thead>
<tbody>
<tr>
<td>B.O.D. (5 days, 20°C)</td>
<td>Not more than 20 p.p.m.</td>
</tr>
<tr>
<td>Suspended solids (plus dissolved iron as Fe)</td>
<td>Not more than 30 p.p.m.</td>
</tr>
<tr>
<td>pH value</td>
<td>Not more than 9 or less than 6</td>
</tr>
<tr>
<td>Cyanide (as HCN)</td>
<td>Not more than 0.1 p.p.m.</td>
</tr>
<tr>
<td>Sulphide (as H₂S)</td>
<td>Not more than 0.1 p.p.m.</td>
</tr>
<tr>
<td>Chromium and other toxic metals either singly or in combination</td>
<td>Not more than 0.5 p.p.m.</td>
</tr>
<tr>
<td>Oil and grease</td>
<td>Nil</td>
</tr>
</tbody>
</table>

In connection with these standards, which are normally imposed (together with a maximum rate of discharge) in consents issued under Section 7 of the 1951 Act, the Board makes the following comments\textsuperscript{37}:

**B.O.D. and suspended solids standards**

'The oxygen-depleting or silting effect of an effluent is not usually immediate in its action and in most rivers is delayed until thorough mixing has taken place. It is therefore considered safe to rely on the full dilution available in the case of oxygen absorbing substances with a normal velocity coefficient and suspended solids which do not settle rapidly.'

**Toxic substances**

'Those substances which have a toxic effect on living organisms in a stream are usually rapid in their action and the occurrence of high local concentrations in a river may be a serious matter. The mixing of an effluent with river water is frequently prolonged.... For the reasons given it is considered unsafe to rely on dilution in the case of toxic substances and, therefore, the limit for the effluent should not exceed the safe limit for the stream.'

Many manufacturers accustomed to reports of analytical results in percentages are apt to think not only that mere traces of metallic and other constituents in effluents are of little significance but also
that water analysts are unnecessarily fussy when they express their results in parts per million. As, however, Sandell has justifiably pointed out, the word 'trace' used in a chemical sense originally signified either an amount too small to estimate or a negligible quantity not worth determining. Today, the word has lost its former meanings partly because more sensitive methods are now available for estimating 'traces' and partly because the so-called traces may, and in fact do, have a profound influence on biological life in streams. Thus, as little as 0·03 p.p.m. of cyanide (expressed as CN) can prove hazardous to fish; 0·1 p.p.m. of copper can destroy algae and other vegetable life; and the presence of a few parts per 1000 million of phenols in a river water can lead to complaints of tastes and odours if the water is subsequently disinfected by chlorination. Small amounts of toxic substances in a trade waste may be harmful because they tend to destroy the micro-organisms upon which the self-purifying powers of a stream depend.

Instead of specifying a large number of chemical standards for toxic substances in industrial wastes (which have the disadvantage that the toxicity of some substances can be reinforced or reduced by the presence of others), it has been suggested that it might be better to introduce a standard routine fish toxicity test. Unfortunately, the formulation of a routine test of this kind is beset with many difficulties (cf. Chapter 9, page 339). In the absence of such a test it would, on the whole, be simpler at the present time to prescribe chemical standards based on the known approximate tolerance of fish to the various toxic substances as determined by careful fish toxicity studies carried out by research workers of repute. Where it is thought that a limited number of chemical standards may prove insufficient for the protection of a fishing stream, it might be wise, pending the introduction of a standard fish toxicity test, to include (e.g. in a Section 7 consent) a protective condition such as the following: 'The effluent shall not contain any liquid or solid matter to such an extent as to cause the specified stream to be poisonous or injurious to fish or the spawning grounds, spawn or food of fish.' A clause of this kind occurs in Sub-section (1) of Section 8 of the Salmon and Freshwater Fisheries Act, 1923 (see Chapter 2).

Despite the many difficulties of carrying out fish toxicity tests or 'bioassays', in the U.S.A. the Aquatic Life Advisory Committee of the Ohio River Valley Water Sanitation Commission has recommended that bioassays should be carried out on trade wastes containing toxic substances and that the results should be expressed as the 'median tolerance limit', i.e. the concentration of substance or waste which kills 50 per cent of the test animals (e.g. fish) after a specified time of exposure (e.g. 48 hours) in laboratory tests. As a
general rule, it is suggested that the final concentration of toxic substance or waste in the receiving stream should not exceed one-tenth of the median tolerance limit. The factor of 0·1 may, it is suggested, be varied in special cases if investigations show that this is necessary. The procedures for conducting these bioassays are given in a publication of a committee of the Federation of Sewage and Industrial Wastes Associations.

In concluding this section on standards for trade wastes, the author would like to lay particular stress on the importance of the dilution factor in the case of industrial effluents discharging to comparatively small streams. A sewage effluent complying with the Royal Commission B.O.D. standard of 20 p.p.m. must receive dilution with at least 8 volumes of clean river water so as to give a stream which does not cause nuisance. Since trade wastes cannot as a rule be purified to the same standard as a sewage effluent (cf. page 559) it is obvious that they must, after discharge, receive dilution in the stream with very much more than 8 volumes of clean river water in order to give a reasonably clean stream; in general, it will be found that some 20 or more volumes of clean river water will be required, the amount depending on the oxygen demand of the effluent.

The reader who is interested in effluent standards will find valuable discussions in several recent papers.

ADDENDUM

Section 46 (i) of the Hertfordshire County Council (Colne Valley Sewerage) Act, 1937

All sewage (including storm and other waters) . . . shall be so treated that the effluent . . . shall conform to the following standard of purity:

(a) The effluent shall not contain more than 3 parts of suspended matter per 100,000 parts and (including its suspended matters) it shall not take up more than 2 parts of dissolved oxygen per 100,000 parts in 5 days at a temperature of 65° F.

(b) The effluent shall comply with the incubator test for putrescibility, that is to say the effluent when incubated for a period of 5 days at a temperature of 80° F in a completely filled and closely-stoppered bottle (of not less than 125 ml. capacity) shall be free from offensive odour and shall not become dark coloured.

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CHAPTER 15

PRESENT AND FUTURE STATUS OF RIVER POLLUTION

Without adequate amounts of reasonably pure water, our present civilization, based as it is on the survival of our national industries, would be in great danger of collapse. The wastage due to pollution of so much of the water of our rivers is, therefore, greatly to be deplored. As we have seen in earlier chapters (see for example Chapters 3 and 4), the main causes of the unsatisfactory state of many of the rivers in this country and in other lands are the discharge to the streams of untreated or imperfectly treated sewage and industrial wastes, a state of affairs which has been gaining ground since the beginning of the Industrial Revolution nearly 200 years ago (see Chapter 1).

In the preceding chapters, the different kinds of pollution affecting rivers have been discussed, the causes have been examined, the bad effects have been considered, and methods available for the abatement of pollution have been reviewed. Despite, however, the vast amount of scientific knowledge that has accumulated, especially during the past 50 years, the problem of the contamination of the rivers of our country and many other lands still remains acute today. The discerning reader may well wonder why, especially since the passing of the Rivers (Prevention of Pollution) Act, 1951, this pollution still continues. Although no short answer to this question can be given, perhaps a brief review of the many difficulties associated with the control of stream pollution may assist the reader in getting a clearer understanding of what is a very complex matter.

The problem of the treatment of domestic sewage to give an effluent which will not pollute a stream has been solved from a technical standpoint (see Chapter 12) but, in practice, sewage can still cause stream pollution in the following cases:

MR A. ERNEST MARPLES, M.P. From speech in House of Commons, July 1953
PRESENT AND FUTURE STATUS

(a) Septic tank installations in uncover areas. The discharge into small streams of unsatisfactory septic tank effluents from isolated property causes considerable pollution in many rural areas (see Chapter 4).

(b) Storm overflows which are improperly or inadequately set. On a combined sewerage system, storm overflows on sewers, which should only come into operation when heavy rain causes the flow of sewage in the sewer to exceed 6 (or more) x D.W.F., are the cause of much pollution in wet weather since they often come into operation with much smaller flows (see Chapter 4).

(c) Badly designed sewage disposal works. An example is a works where sludge drying facilities are inadequate.

(d) Overloaded sewage disposal works.

(e) Sewage disposal works subject to mining subsidence. When a sewage works is situated in a mining area where considerable subsidence occurs, any damage to the sewers, tanks, etc., may lead to untreated sewage finding its way to the nearest stream (see Chapter 4).

Overloaded sewage works, in general, cause by far the most widespread pollution. Many of these overloaded works are of insufficient capacity and in some instances are dealing with as much as two or three times the flow for which they were originally designed. Sewage flows in this country are tending to increase not only because of the construction of new housing estates and the connection of larger volumes of sewage and trade wastes to the sewers but also on account of the rise in the domestic usage of water due to changes in the habits and standards of living of the people. As a result, in England, new sewage works are now usually designed on the basis of about 40–45 gal. of domestic sewage per head of population served per day* instead of on the former basis of about 25–30 gal. This means that the sewage works of today must be correspondingly larger and therefore more expensive to construct.

Local authorities are, as a rule, anxious to improve their sewage works but new sewage schemes and extensions to old sewage works require authorization by the Ministry of Housing and Local Government and loans for such schemes are only granted by the Ministry after a local public inquiry has been held by an inspector of the Ministry. The rate of interest charged by the Public Works Loan Board to local authorities requiring loans for carrying out public works, including sewerage schemes, has been increased several times recently (it is now 5 per cent on loans for more than 5 years) thus adding an extra burden to sewage works construction.

* In Scotland, where the water consumption is higher, this figure may be as high as 60 gal.
costs which are already inflated by present-day high prices and high labour costs. Unfortunately, owing to the financial difficulties of the times and the continued need for economy in public spending, schemes for the extension or reconstruction of overloaded sewage works are delayed or whittled down by Government restrictions on capital expenditure. This attitude of the Ministry towards sewage disposal works is probably the biggest single factor today contributing to the continuing pollution of some of the rivers of this country. Many important sewerage schemes must remain on paper for some years because the Ministry will not sanction the necessary loan and as a result constructional work at a great many sewage disposal plants is not keeping pace with housing and industrial developments. The authorization of many of these schemes would be a major step in the battle against pollution.

In general, trade wastes should be discharged to the sewers of a local authority and subsequently treated with sewage at a sewage disposal works. This is usually the best method if the sewage works is of adequate capacity but, unfortunately, for various reasons fully discussed previously (see Chapter 13), this convenient method is not always possible. In such cases, it may be necessary to discharge the wastes to a stream, and although treatment of the wastes by the manufacturer at a trade effluent treatment plant is always demanded by the river board, it is not always financially practicable, even with the best will in the world and using the best scientific methods, to produce a final effluent comparable in quality with a Royal Commission sewage effluent. Hence, even a treated industrial effluent can cause considerable pollution, particularly if the dilution afforded by the receiving stream is low. There are some trade wastes for which no reasonably practicable methods of treatment giving a satisfactory effluent are known. For example, gas works effluents, certain kier liquors and tannery wastes (see Chapter 13), but this does not imply that these waste waters cannot be substantially improved by some form of treatment. If, therefore, disposal of these intractable wastes to a sewage works is not feasible, discharge to a river may be unavoidable and consequently much pollution will take place. In some instances, where a factory is situated in a built-up area and is surrounded by other buildings, there may be considerable difficulty in finding a suitable site for tipping sludge and other semi-solid or solid waste materials produced either in the manufacturing process or in the treatment of the effluents. The shortage of man-power in these days of full employment also adds to the difficulties facing manufacturers in running a trade effluent treatment plant and producing a satisfactory effluent. It must be remembered, too, that we live in a changing world for which the advances in science are to a large extent responsible. Industry
is continually altering its processes and so producing new types of effluent. In particular, the chemical industry has, during the past 25 years or so, provided us with many new effluent problems through the introduction of such novel products as DDT and other insecticides, penicillin, sulpha drugs, plastics and terylene. Again, new industrial processes may undergo modifications in the course of time either because they are no longer profitable or on account of more recent discoveries. Hence, a trade effluent treatment plant producing a satisfactory effluent today may well become out of date and unsuitable for the task in a few years' time. Moreover, new industries can create entirely new industrial waste problems which may take considerable time and financial expenditure to solve. Although, therefore, under the 1951 Act it is a punishable offence to discharge to a river anything ‘noxious, poisonous, or polluting’, in practice a loophole in the Act does exist; if there is nowhere for an effluent to go except to a river and if all reasonably practicable means of purification are being adopted, then the law permits the discharge to the river even if pollution is thereby caused.

Many traders are obliged to use poisonous chemicals in their manufacturing processes; for instance, in electroplating, chromates and other toxic metallic compounds and cyanides are indispensable. It is a pity that in many cases greater care is not taken in the use and disposal of such dangerous chemical compounds. In recent years, carelessness in handling cyanides and cyanide waste waters has resulted in a number of quite unnecessary cases of fish mortality in British rivers. For instance, the Severn River Board has reported that during the week ending 31 May 1952, the fish in the River Severn for a distance of 17 miles below Newtown and in the Shropshire Union Canal for 10 miles were annihilated by a cyanide discharge. The report goes on to say:

‘The cyanide pollution was not an isolated one. The light-hearted way in which industry often treats one of the most poisonous chemicals known is astonishing. In more than one instance, not only the work-people but the management claimed to have been quite unaware that they were using cyanide.’

We will now consider some of the ways whereby the difficulties connected with the pollution problem can be obviated. There is little doubt that much unnecessary pollution by imperfectly treated sewage could be avoided by the expenditure of more money on the extension and modernization of overloaded sewage disposal works. Wherever possible, trade wastes should be connected to the local sewers, if necessary after pre-treatment, and treated in admixture with sewage at a sewage works. A modern tendency is the
formation of joint sewerage boards or regional sewage boards for the purpose of centralizing the treatment of sewage. In many areas where there are a number of small unsatisfactory sewage works which are unable to deal with trade wastes, it is often better to replace the small works by a large regional works. This reduces the number of points of pollution and by bringing large volumes of sewage to one works enables more trade waste to be accepted and dealt with properly. A large works also has the advantage over the small works of being able to afford the necessary skilled technical supervision. Under Section 9 of the 1951 Act (see Chapter 2) the Minister of Housing and Local Government has the power to make an order requiring the sewage from one local authority to pass into the sewers of another.

Firms setting up new factories producing trade effluents should look ahead and pay much more attention to the design, layout and siting of the factory and, in particular, avoid selecting sites far from public sewers or sites which are cramped or otherwise unsuitable for the construction of an adequate treatment plant. In the past, far too many factories have been built without any consideration for effluent treatment problems. In this connection, Henkel\(^3\) states that the du Pont Company in the U.S.A. do not authorize the construction of plant for any new chemical process producing liquid effluents unless provision has been made in the design for the proper treatment of the wastes. Much unnecessary pollution could be avoided if all industrial undertakings adopted this public-spirited attitude.

There is little doubt that more intensive research on methods of treating and purifying the common trade-waste waters will be of great assistance in the alleviation of stream pollution. It is to be hoped that much more work of this nature will be undertaken by the great industrial research associations who have unrivalled facilities and financial means at their disposal for such investigations. The Joint Research Committee of the Gas Council and the University of Leeds have carried out and are still doing much valuable research work on the very difficult problem of the treatment of effluents from gas works. Much important research has been carried out in the past by the Water Pollution Research Laboratory under its able and energetic director, Dr B. A. Southgate, C.B.E., and now that this laboratory has moved to a large, new, and well-equipped building at Stevenage, Herts\(^4\), and has increased its staff, it will be possible to expand the programme of work and carry out fundamental investigations of the basic processes used for the treatment of sewage and trade wastes. The possibility of breaking down biologically substances found in trade wastes by utilizing specialized micro-organisms is being studied\(^5\) and has
already achieved some success in the case of cyanide (see Chapter 13, page 515).

There is no doubt that most industrialists as well as the large nationalized undertakings do realize the important part they can play in co-operating with river boards in the task of improving the condition of our industrial rivers, and it is only a very small minority that may have to be dealt with by legal action. As Hoak has wisely said: 'The most effective tool of anti-pollution administrators is education—not the threat of legal reprisal.' Much advice and information to manufacturers about legal and technical matters connected with the treatment and disposal of waste waters from industrial premises in this country are to be found in a useful little booklet published by the Federation of British Industries.

The question of the pollution of tidal waters in this country has only received passing mention in this book as the 1951 Act only applies to inland streams (i.e. non-tidal waters) except in those rare cases in which the Minister has, by statutory order, extended the provisions of the Act to tidal waters (cf. Chapter 13, page 496). The appallingly bad condition of many of our tidal rivers and estuaries owing to gross pollution by sewage and trade wastes has been graphically described by Turner in a series of booklets published by the British Field Sports Society. In many cases, towns of considerable size are permitting large volumes of untreated or partially-treated sewage to pass to estuaries, and factories and gas works are discharging a great variety of trade wastes containing substances such as cyanides, toxic metals, phenols and other chemical compounds, which are highly toxic to fish life. It is not surprising, therefore, that in many estuaries there is a pollution barrier of deoxygenated or contaminated water which effectively prevents the passage of such migratory fish as salmon. Unfortunately, mixing of water and effluent in an estuary is rarely perfect, not only on account of the peculiarity of the ebb and flow of the tide as affected by the physical characteristics of the estuary but also because of the differing densities and temperatures of fresh water and salt water. The old theory that polluting matter is carried out to sea on the ebb tide and does not return on the next flood tide is now known to be contrary to experience in many instances.

The complicated problem of the pollution of estuaries is now receiving much attention both in the U.S.A. and Britain. The reader who is interested in recent work on the calculation of the distribution of salinity within an estuary, of the extent to which sea water and fresh water mix in an estuary, and on the evaluation of the extent to which polluting matter is dispersed in tidal waters, should refer to the work of Ketchum and Predy.

The river pollution problem is not one that is going to be solved
in a few years but calls for long-continued patient efforts by those concerned. There is, indeed, no easy solution. Tact and diplomacy on the part of the river boards, goodwill and co-operation on the part of the local authorities and manufacturers and, shall we say, a less parsimonious attitude on the part of the Ministry will in the long run transform the streams and watercourses of this country beyond recognition and so rectify the damage done by the Industrial Revolution. Many enthusiastic anglers would like to see all our polluted industrial rivers become fishing streams of rippling purity. All of us, of course, will agree that clean rivers are most desirable from the standpoint of public health, for aesthetic reasons, and because the demand for reasonably clean water for industrial and domestic purposes is becoming more urgent. But it is extremely doubtful whether certain overburdened industrial rivers, especially in the densely-populated areas of Lancashire, the West Riding of Yorkshire, and the Midlands will ever become really clean and capable of supporting fish life. The River Irwell*, for example, consists mainly of sewage effluents and trade effluents in dry weather so even if all these effluents were 'satisfactory', judged by certain arbitrary standards, the river could never be brought up to the standard of a fishing stream because of the absence of sufficient clean diluting water. Mr H. C. Gilson, director of the Freshwater Biological Association, has indeed stated that it would be fantastically expensive to reclaim the River Irwell or any other industrial river and that, to quote his words, 'it is essential that some rivers should be regarded purely as drains'. So long as this country remains predominantly industrial—and industry is likely to be its life-blood for as long as we can foresee—manufacturers must be permitted to discharge their effluents, treated by the best practicable means, to the rivers if no other means of disposal is available.

An important factor tending to intensify pollution of our rivers must not be overlooked. The ever-increasing demands made on rivers by domestic users and by industrial undertakings are likely to accentuate the difficulties of pollution prevention for the result can only be a larger proportion of sewage effluents and trade effluents in the rivers and a smaller proportion of clean water.

Wilson has made the interesting suggestion that river authorities in certain areas of Britain might well consider ways of intensifying the self-purification of streams and so help to reduce the pollution load. He suggests that this might be done by construction, at certain points along the river valley, of impounding lakes

* Including discharges to its tributaries, there are 83 sewage works and 190 trade premises discharging effluents to this comparatively small and much overburdened Lancashire river, which has been well described as the hardest worked stream in the country.
where storage for sufficiently long periods would improve the water; this has actually been done in connection with the River Ruhr in Germany (see Chapter 12, page 425). An alternative method recommended by Wilson is the setting up of river purification plants which might consist of aeration units, built at the side of the stream or even in the stream itself, the purpose of which is to increase the amount of dissolved oxygen in the water and thereby accelerate the oxidation of organic matter through the agency of micro-organisms. This proposal is not merely a theoretical speculation since work on artificial aeration has actually been carried out with some measure of success in the U.S.A. in the case of a stream polluted by sulphite waste liquor.

Dr A. Key, Senior Chemical Inspector to the Ministry of Housing and Local Government, has suggested that the problem of river pollution in this country will never be completely solved since, with the growth of population and of new manufacturing processes, new effluent difficulties will arise which will take much time, money and research to overcome. As illustrations, he mentions three new problems with us today which have not yet been solved and which hardly existed at all at the beginning of the World War II, namely

(i) Radioactive effluents (see Chapter 13, page 529).
(ii) Chemicals used in agriculture (insecticides, weed-killers, fungicides, etc.), many of which are very toxic to fish in small amounts (see Chapter 4, pages 84-5).
(iii) Synthetic detergents (see Chapter 3, pages 42-7).

It might be argued that eventually science will find a way of dealing with the majority of the intractable pollution problems, but this is bound to take a considerable time and by then new problems will have arisen. Moreover, pollution may still occur owing to accidents and mechanical faults in plant installations and through unforeseeable human errors and limitations which are quite in-calculable. This does not mean that we should sit back and do nothing. Rather should river boards and all concerned in anti-pollution work redouble their efforts to restore the wholesomeness of those streams which might well become fishing streams again and improve those rivers in manufacturing areas which at present are little better than open sewers.

In conclusion, it can be stated that although there is little doubt that through the combined efforts of river boards, local authorities, the large nationalized undertakings, and the manufacturers, much will be done to alleviate the pollution of streams, the most that can be expected with a large number of grossly-polluted rivers flowing through highly industrialized areas is a marked reduction in the
pollution. Indeed, the available evidence put forward in this chapter, and discussed throughout this book, suggests that pollution, like crime, disease, and road accidents, will eventually be brought under better control but will never be completely eliminated. And it must be emphasized that river purification is bound to involve heavy financial expenditure. Any major improvements in the condition of our rivers can only be brought about gradually; they will have to be paid for in the long run by the general public out of taxation, by increases in municipal and county rates in those areas and districts where new sewage disposal works are constructed or extensions to old works are carried out, and by price increases in commodities in those cases where a manufacturer has to construct an expensive trade effluent treatment plant or to pay for the treatment of his wastes by the local authority. But against this must be set the large sums of money which are being spent at present by water undertakings and industrial concerns on the treatment of water taken from the heavily-polluted streams.

Finally, it must be stressed that the prevention of river pollution is not a cranky idea or a fad but is an absolute necessity, especially in the case of a densely-populated and highly-industrialized country, for the maintenance of public health, industrial efficiency, and general amenities.

Coleridge, speaking of the pollution of the River Rhine in 1828 in his poem on *Cologne* asks

"But tell me, Nymphs, what power divine
Shall henceforth wash the river Rhine?"

The River Boards by pursuing an energetic policy can, in spite of the many difficulties and obstacles, do much to assist the poet’s ‘power divine’ and so pave the way for a return to the former glories of at least the majority of our rivers so that in the words of Izaak Walton (The Compleat Angler) all who wish may ‘be quiet, and go a-angling’.

REFERENCES

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3 HENKEL, H. O., ‘Surface and underground disposal of chemical wastes at Victoria, Texas’, *Sewage Ind. Wastes*, 25 (1953) 1044
4 ‘New Water Pollution Research Laboratory’, *J. Inst. Chem.*, 78 (1954) 589-41
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13 GILSON, H. C., Manchester Guardian, 17 June 1954, p. 5
14 WILSON, H., 'Final treatment of sewage effluent'. The River Boards' Association Year Book, 1954, pp. 45-95
15 TYLER, R. G., 'Polluted streams cleared up by aeration', Gt. Engng, Easton, Pa, 16 (1946) 348. Also Summ. curr. Lit. Wat. Pollut., 19 (1946) 304
APPENDIX

The following table of saturation values for dissolved oxygen, reproduced here by kind permission of the Director, has been compiled from recent data obtained by the Water Pollution Research Laboratory, assuming air at 100 per cent humidity and under a total pressure of 760 mm of mercury. Each entry is correct to the nearest digit. The data are calculated for air, free from carbon dioxide, and containing 20.93 per cent of oxygen.

Table 107. Solubility of oxygen in water. Dissolved oxygen. Saturation values for fresh water and mixtures of fresh water and sea-water. Milligrams of oxygen dissolved in 1 l. of water saturated with air at the stated temperatures under a pressure of 760 mm.

<table>
<thead>
<tr>
<th>Temp. °C</th>
<th>Chloride, in p.p.m. of Cl</th>
<th>Dissolved oxygen in mg/l.</th>
<th>Difference per 100 p.p.m. of Cl mg/l.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
<td>5000</td>
<td>10,000</td>
</tr>
<tr>
<td>0</td>
<td>14-16</td>
<td>13-40</td>
<td>12-64</td>
</tr>
<tr>
<td>1</td>
<td>13.77</td>
<td>13.03</td>
<td>12.30</td>
</tr>
<tr>
<td>2</td>
<td>13.40</td>
<td>12.68</td>
<td>11.97</td>
</tr>
<tr>
<td>3</td>
<td>13.05</td>
<td>12.36</td>
<td>11.66</td>
</tr>
<tr>
<td>4</td>
<td>12.70</td>
<td>12.03</td>
<td>11.34</td>
</tr>
<tr>
<td>5</td>
<td>12.37</td>
<td>11.72</td>
<td>11.06</td>
</tr>
<tr>
<td>6</td>
<td>12.06</td>
<td>11.43</td>
<td>10.79</td>
</tr>
<tr>
<td>7</td>
<td>11.76</td>
<td>11.14</td>
<td>10.53</td>
</tr>
<tr>
<td>8</td>
<td>11.47</td>
<td>10.87</td>
<td>10.28</td>
</tr>
<tr>
<td>9</td>
<td>11.19</td>
<td>10.61</td>
<td>10.05</td>
</tr>
<tr>
<td>10</td>
<td>10.92</td>
<td>10.36</td>
<td>9.80</td>
</tr>
<tr>
<td>11</td>
<td>10.67</td>
<td>10.12</td>
<td>9.58</td>
</tr>
<tr>
<td>12</td>
<td>10.43</td>
<td>9.90</td>
<td>9.37</td>
</tr>
<tr>
<td>13</td>
<td>10.20</td>
<td>9.68</td>
<td>9.17</td>
</tr>
<tr>
<td>14</td>
<td>9.98</td>
<td>9.48</td>
<td>8.98</td>
</tr>
<tr>
<td>15</td>
<td>9.76</td>
<td>9.27</td>
<td>8.78</td>
</tr>
<tr>
<td>16</td>
<td>9.56</td>
<td>9.08</td>
<td>8.61</td>
</tr>
<tr>
<td>17</td>
<td>9.37</td>
<td>8.91</td>
<td>8.44</td>
</tr>
<tr>
<td>18</td>
<td>9.18</td>
<td>8.73</td>
<td>8.26</td>
</tr>
<tr>
<td>19</td>
<td>9.01</td>
<td>8.57</td>
<td>8.13</td>
</tr>
<tr>
<td>20</td>
<td>8.84</td>
<td>8.41</td>
<td>7.98</td>
</tr>
<tr>
<td>21</td>
<td>8.68</td>
<td>8.26</td>
<td>7.83</td>
</tr>
<tr>
<td>22</td>
<td>8.53</td>
<td>8.12</td>
<td>7.70</td>
</tr>
<tr>
<td>23</td>
<td>8.38</td>
<td>7.97</td>
<td>7.57</td>
</tr>
<tr>
<td>24</td>
<td>8.25</td>
<td>7.85</td>
<td>7.45</td>
</tr>
<tr>
<td>25</td>
<td>8.11</td>
<td>7.72</td>
<td>7.33</td>
</tr>
<tr>
<td>26</td>
<td>7.99</td>
<td>7.61</td>
<td>7.22</td>
</tr>
<tr>
<td>27</td>
<td>7.86</td>
<td>7.48</td>
<td>7.10</td>
</tr>
<tr>
<td>28</td>
<td>7.75</td>
<td>7.37</td>
<td>7.00</td>
</tr>
<tr>
<td>29</td>
<td>7.64</td>
<td>7.27</td>
<td>6.94</td>
</tr>
<tr>
<td>30</td>
<td>7.53</td>
<td>7.16</td>
<td>6.89</td>
</tr>
</tbody>
</table>
If the barometric pressure is markedly different from 760 mm, the solubility of oxygen can be calculated from the formula:

\[
S' = \frac{P}{760} S
\]

where \( S' \) = solubility of oxygen at \( P \) mm pressure and \( S \) = solubility of oxygen at 760 mm pressure (from above table).

### Table 108. Interconversion of British, American and metric units

<table>
<thead>
<tr>
<th>Area</th>
<th>1 in.</th>
<th>= -2.54 cm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1 ft.</td>
<td>= 0.3048 m</td>
</tr>
<tr>
<td></td>
<td>1 mile</td>
<td>= 1.6093 km</td>
</tr>
<tr>
<td></td>
<td>1 m</td>
<td>= 3.93701 in.</td>
</tr>
<tr>
<td>Weight</td>
<td>1 sq. ft = 929.03 cm²</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 acre</td>
<td>= 4840 yd² = 0.4047 hectares</td>
</tr>
<tr>
<td></td>
<td>1 sq. mile</td>
<td>= 640 acres = 229 hectares</td>
</tr>
<tr>
<td></td>
<td>1 hectare</td>
<td>= 10,000 m² = 2.471 acres</td>
</tr>
</tbody>
</table>

| Volume and capacity | 1 ft.³ | = 0.2688 imperial gal. = 28.316 L |
|                     | 1 imperial gal. | = 4.539960 L = 0.001337 m³ |
|                     | 1 U.S. gal. | = 0.833 imperial gal. |
|                     | 1 m³ | = 1000 imperial gal. |
| Pressure            | 1 atm | = 1.01325 bar |
|                     |       | = 1013.25 millibars |
|                     |       | = 29.921 in. of mercury |
|                     | 1 bar | = 1000 millibars |
|                     |       | = 14.696 in. of mercury |
|                     |       | = 1.01325 bar|
|                     |       | = 29.921 in. of mercury |
| Velocity            | 1 ft./sec | = 0.06818 m.p.h. = 0.907 km/hour |
|                     | 1 m.p.h. | = 1.467 ft./sec = 0.88 ft./min |
| Flow of water       | 1 ft./sec (1 cusec) | = 538.170 imperial gal. per 24 hours |
|                     |       | = 696.300 U.S. gal. per 24 hours |
|                     |       | = 1099 L per 24 hours |
|                     |       | = 1.7 m³/hour |

[For approximate work, it may be assumed that]

|                 | 1 cusec | = 500,000 imperial gal/day |
|                 |         | = 1700 L/min |
| and that        | 1 ft./min | = 9000 imperial gal/day |
|                 |         | = 1.7 m³/hour |
|                 | 1 m³/hour | = 0.00891 ft./sec |
|                 |         | = 0.0000686 cusec |

* Board of Trade definition.  † 0 ° C and standard gravity.
APPENDIX

Table 109—cont.

Miscellaneous data
1 in. of rain over 1 acre = 22,624 imperial gallons = 101 tons (approx.)
1 in. of rain over 1 sq. mile = 64,640 tons (approx.)

Table 109. Conversion table for concentration units

<table>
<thead>
<tr>
<th>Grains per imperial gal.</th>
<th>Parts per 100,000</th>
<th>Grammes per million millilitres</th>
<th>Milligrammes per litre</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Grams per litre</td>
<td>p.p.m.</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>(parts per million)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>specific gravity</td>
<td></td>
</tr>
<tr>
<td>0.7</td>
<td>1,425</td>
<td>14.25</td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>1</td>
<td>1</td>
<td></td>
</tr>
</tbody>
</table>

In the case of samples with a specific gravity significantly greater than 1 (e.g. brines, sea-water, slurries, etc.), ‘parts by weight per million parts by weight’ is not the same as ‘parts by weight per million parts by volume’, but is given by the expression:

parts by weight per million parts by weight = \( \frac{\text{milligrammes per litre}}{\text{specific gravity}} \)

Table 110. Conversion table for hardness

<table>
<thead>
<tr>
<th>German</th>
<th>0.07</th>
<th>0.056</th>
</tr>
</thead>
<tbody>
<tr>
<td>French</td>
<td>0.07</td>
<td>1</td>
</tr>
<tr>
<td>&quot;</td>
<td>1.25</td>
<td>17.8</td>
</tr>
</tbody>
</table>

German degrees of hardness are expressed in terms of CaO (each degree of hardness = 1 part of CaO per 100,000 parts of water). All the other degrees of hardness are expressed in terms of CaCO3.

Table 111. Water: relation between weight and volume

Official definitions
10 lb. (avoir.) distilled water (62° F, 30 in. mercury pressure) occupies 1 imperial gal.
1 kg. distilled water (4° C, 760 mm mercury pressure) occupies 1 l.

Approximate relationships
1 ton = 224 imperial gal. = 35.94 ft.3 = 1.066 m.3
1 fl.3 = 62.5 lb. = 0.0278 ton
1 m.3 = 1000 kg = 1 metric ton = 220 gal. = 0.9842 ton
ASPECTS OF RIVER POLLUTION

Table 112. Sea-water: approximate weight-volume relations

<table>
<thead>
<tr>
<th>Imperial gallon</th>
<th>10.26 lb.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 fl. j.</td>
<td>0.0285 ton</td>
</tr>
<tr>
<td>1 ton</td>
<td>219 gal.</td>
</tr>
</tbody>
</table>

Table 113. Conversion factors for gases

<table>
<thead>
<tr>
<th>Multiply</th>
<th>By</th>
<th>To obtain</th>
</tr>
</thead>
<tbody>
<tr>
<td>p.p.m. of oxygen</td>
<td>0.608</td>
<td>ml/l.</td>
</tr>
<tr>
<td>ml/l. of oxygen</td>
<td>1.43</td>
<td>p.p.m.</td>
</tr>
<tr>
<td>p.p.m. of carbon dioxide</td>
<td>0.506</td>
<td>ml/l.</td>
</tr>
<tr>
<td>ml/l. of carbon dioxide</td>
<td>1.98</td>
<td>p.p.m.</td>
</tr>
</tbody>
</table>

In general, British and American units are virtually the same. When comparing British and American results, the differences shown in the following table should be noted.

Table 114. Differences in British and American units

<table>
<thead>
<tr>
<th>British units</th>
<th>American units</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 gal. of water weighs 10 lb.</td>
<td>1 gal. of water weighs 8.33 lb.</td>
</tr>
<tr>
<td>1 gal. = 277.4 in.³ = 4.546 l.</td>
<td>1 gal. = 231 in.³ = 3.785 l.</td>
</tr>
<tr>
<td>1 ton = 2240 lb.</td>
<td>1 ton = 2000 lb.</td>
</tr>
</tbody>
</table>

Table 115. Alkalinity conversion factors

<table>
<thead>
<tr>
<th>Multiply</th>
<th>By</th>
<th>To get</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO₃</td>
<td>0.98</td>
<td>H₂SO₄</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.8</td>
<td>NaOH</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.74</td>
<td>Ca(OH)₂</td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.66</td>
<td>Ca</td>
</tr>
<tr>
<td>Ca(OH)₂</td>
<td>1.35</td>
<td>CaCO₃</td>
</tr>
</tbody>
</table>

Table 116. Chemical volumetric factors for use in titrations

| Free chlorine | 1 ml. N/40 sodium thiosulphate | = 0.887 mg chlorine |
| Sulphate      | 1 ml. N/40 sodium thiosulphate | = 0.420 mg H₂SO₄ |
| Permanganate value | 1 ml. N/40 sodium thiosulphate | = 0.2 mg oxygen |
| Dissolved oxygen | 1 ml. N/40 sodium thiosulphate | = 0.1 mg oxygen |
| Chromate      | 1 ml. N/40 sodium thiosulphate | = 0.43 mg Cr  |
| Copper        | 1 ml. N/10 sodium thiosulphate | = 0.357 mg copper |
| Phenol        | 1 ml. N/10 sodium thiosulphate | = 1.90 mg phenol |
| Iron          | 1 ml. N/100 potassium dichromate | = 0.558 mg iron |
| Cyanide       | 1 ml. N/100 silver nitrate | = 0.54 mg HCN |
| Calcium       | 1 ml. N/100 potassium permanganate | = 0.2 mg Ga  |
|               | 1 ml. N/80 potassium permanganate | = 0.25 mg Ca  |
### Table 117. Conversion of Centigrade to Fahrenheit and Fahrenheit to Centigrade temperature,

\[
\begin{align*}
S = \frac{9}{5} \\
\text{Each } ^\circ \text{C rise} &= 1 \frac{\circ}{5} \text{F rise} \\
\text{Each } ^\circ \text{F rise} &= \frac{5}{9} \text{C rise}
\end{align*}
\]

<table>
<thead>
<tr>
<th>Centigrade to Fahrenheit</th>
<th>Fahrenheit to Centigrade</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>°F</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>0</td>
<td>32.0</td>
</tr>
<tr>
<td>1</td>
<td>35.8</td>
</tr>
<tr>
<td>2</td>
<td>39.2</td>
</tr>
<tr>
<td>3</td>
<td>42.8</td>
</tr>
<tr>
<td>4</td>
<td>46.4</td>
</tr>
<tr>
<td>5</td>
<td>48.8</td>
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<tr>
<td>6</td>
<td>52.0</td>
</tr>
<tr>
<td>7</td>
<td>55.6</td>
</tr>
<tr>
<td>8</td>
<td>59.2</td>
</tr>
<tr>
<td>9</td>
<td>62.8</td>
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<tr>
<td>10</td>
<td>66.0</td>
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<tr>
<td>11</td>
<td>69.8</td>
</tr>
<tr>
<td>12</td>
<td>73.4</td>
</tr>
<tr>
<td>13</td>
<td>77.0</td>
</tr>
<tr>
<td>14</td>
<td>79.2</td>
</tr>
<tr>
<td>15</td>
<td>81.6</td>
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<td>16</td>
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<td>17</td>
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<td>18</td>
<td>89.6</td>
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<td>19</td>
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<td>20</td>
<td>95.0</td>
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<td>21</td>
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<td>162.0</td>
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<tr>
<td>54</td>
<td>164.0</td>
</tr>
<tr>
<td>55</td>
<td>166.0</td>
</tr>
<tr>
<td>56</td>
<td>168.0</td>
</tr>
</tbody>
</table>
### Table 118. Analyses of River Irwell on 8 July 1953. (Taken from Mersey River Board, 3rd Annual Report, 1953-4)

Survey of River Irwell taken on 8 July 1953. Trade premises at sampling points 10-17 not working, but sewage disposal works operating. (Annual holidays of Ramclough, Bury, Radcliffe and Little Lever)

**Weather:** Showery. **River flow:** 2 × D.W.F.

<table>
<thead>
<tr>
<th>Sampling point</th>
<th>Location</th>
<th>River temp. °C</th>
<th>pH</th>
<th>M.O.s. from top point</th>
<th>M.E.C. S. of water</th>
<th>Chloride in Cl</th>
<th>O.N.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Above Irwell Springs Printing Co.</td>
<td>10.5°</td>
<td>7.2</td>
<td>0</td>
<td>88</td>
<td>P</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>At Dog Pits Bridge</td>
<td>13.5°</td>
<td>9.6</td>
<td>0.9</td>
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<td>Doubtful</td>
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</tbody>
</table>
### Table 119. Analyses of River Irwell on 7 October 1953. (Taken from Mersey River Board, 3rd Annual Report, 1953-4)

Survey of River Irwell taken on 7 October 1953. Trade pressure working.
Weather: dry for several days. River flows: about dry weather flow.

<table>
<thead>
<tr>
<th>No.</th>
<th>Sampling point</th>
<th>River samp. C</th>
<th>pH</th>
<th>T.S. from sample 1</th>
<th>Alk. equiv. of water</th>
<th>Alk. equiv. and P=maximum P=acid</th>
<th>Chloride + T.S. from KCl (l)</th>
<th>G.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Above Irwell Springs Printing Co.</td>
<td>9.5°</td>
<td>7.0</td>
<td>0</td>
<td>75</td>
<td>P</td>
<td>14</td>
<td>7/1</td>
</tr>
<tr>
<td>2</td>
<td>At Dog Pits Bridge</td>
<td>11.5°</td>
<td>6.8</td>
<td>0.9</td>
<td>67</td>
<td>P</td>
<td>28</td>
<td>60-6</td>
</tr>
<tr>
<td>3</td>
<td>At Cooper Street, Baxey</td>
<td>10.5°</td>
<td>6.2</td>
<td>1.7</td>
<td>77</td>
<td>P</td>
<td>16</td>
<td>13-0</td>
</tr>
<tr>
<td>4</td>
<td>Above confluence with Gorsebrook</td>
<td>10.5°</td>
<td>6.9</td>
<td>5.2</td>
<td>90</td>
<td>P</td>
<td>16</td>
<td>3-0</td>
</tr>
<tr>
<td>5</td>
<td>At Lomondale Bridge, Waterfoot</td>
<td>11°</td>
<td>7.0</td>
<td>5.8</td>
<td>83</td>
<td>P</td>
<td>16</td>
<td>9-4</td>
</tr>
<tr>
<td>6</td>
<td>Above confluence with Linn Water</td>
<td>11.5°</td>
<td>8.0</td>
<td>7.0</td>
<td>56</td>
<td>P</td>
<td>4</td>
<td>32-0</td>
</tr>
<tr>
<td>7</td>
<td>At Towneleyfield Weir</td>
<td>11.5°</td>
<td>8.2</td>
<td>7.6</td>
<td>56</td>
<td>P</td>
<td>4</td>
<td>39-2</td>
</tr>
<tr>
<td>8</td>
<td>Above confluence with River Ogden</td>
<td>12°</td>
<td>6.9</td>
<td>0.7</td>
<td>28</td>
<td>P</td>
<td>26</td>
<td>20-4</td>
</tr>
<tr>
<td>9</td>
<td>At Stubbins Bridge</td>
<td>12°</td>
<td>6.9</td>
<td>11.2</td>
<td>23</td>
<td>P</td>
<td>26</td>
<td>18-0</td>
</tr>
<tr>
<td>10</td>
<td>Above confluence with Holcombe Brook</td>
<td>12.5°</td>
<td>7.0</td>
<td>14.2</td>
<td>30</td>
<td>F 18 h (Hg)</td>
<td>36</td>
<td>32-4</td>
</tr>
<tr>
<td>11</td>
<td>Above B.E.A., Bury intake</td>
<td>13°</td>
<td>7.0</td>
<td>17.0</td>
<td>32</td>
<td>F 6 days (Hg)</td>
<td>36</td>
<td>21-6</td>
</tr>
<tr>
<td>12</td>
<td>At Weir near Danefield Mills</td>
<td>11.5°</td>
<td>7.1</td>
<td>10.7</td>
<td>24</td>
<td>P</td>
<td>40</td>
<td>22-0</td>
</tr>
<tr>
<td>13</td>
<td>Above confluence with River Roch</td>
<td>11.5°</td>
<td>7.1</td>
<td>21.2</td>
<td>32</td>
<td>F 6 days (Hg)</td>
<td>36</td>
<td>21-2</td>
</tr>
<tr>
<td>14</td>
<td>Above confluence with Bealey's Gait</td>
<td>14°</td>
<td>7.1</td>
<td>22.2</td>
<td>33</td>
<td>P</td>
<td>70</td>
<td>19-6</td>
</tr>
<tr>
<td>15</td>
<td>Above Mount San Works</td>
<td>15.5°</td>
<td>7.1</td>
<td>24.0</td>
<td>28</td>
<td>P</td>
<td>74</td>
<td>25-2</td>
</tr>
<tr>
<td>16</td>
<td>Below Mount San Works</td>
<td>15.5°</td>
<td>6.8</td>
<td>24.7</td>
<td>Nil</td>
<td>P</td>
<td>68</td>
<td>36-0</td>
</tr>
<tr>
<td>17</td>
<td>Above confluence with River Cramul</td>
<td>17°</td>
<td>6.6</td>
<td>25.0</td>
<td>Nil</td>
<td>F 7 h (Hg)</td>
<td>72</td>
<td>36-0</td>
</tr>
<tr>
<td>18</td>
<td>At Ringley Bridge</td>
<td>14.5°</td>
<td>6.4</td>
<td>27.1</td>
<td>Nil</td>
<td>P</td>
<td>74</td>
<td>26-0</td>
</tr>
<tr>
<td>19</td>
<td>Above Gibson (Swinton and Prend.—)</td>
<td>20°</td>
<td>8.2</td>
<td>30.0</td>
<td>Nil</td>
<td>F 3 h (Hg)</td>
<td>90</td>
<td>36-0</td>
</tr>
<tr>
<td>20</td>
<td>At Crosswell Bridge, Salind</td>
<td>10.5°</td>
<td>8.0</td>
<td>34.5</td>
<td>Nil</td>
<td>P</td>
<td>80</td>
<td>38-4</td>
</tr>
<tr>
<td>21</td>
<td>Below confluence with River Medlock,</td>
<td>17°</td>
<td>7.0</td>
<td>38.7</td>
<td>Nil</td>
<td>P</td>
<td>82</td>
<td>39-2</td>
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</table>
### Table 119—cont.

<table>
<thead>
<tr>
<th>R.O.D. (15 days, 20°C)</th>
<th>Total solids (as CaCO₃)</th>
<th>Susp. solids</th>
<th>Alkalinity (as CaCO₃)</th>
<th>B.O.D.</th>
<th>Ammoniacal nitrogen</th>
<th>Nitrates</th>
<th>Remarks</th>
<th>Classification</th>
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<tr>
<td>0.6</td>
<td>209</td>
<td>1</td>
<td>140</td>
<td>Nil</td>
<td>0.12</td>
<td>Nil</td>
<td>1/2</td>
<td>Very clean</td>
</tr>
<tr>
<td>48.0</td>
<td>399</td>
<td>27</td>
<td>80</td>
<td>0.08</td>
<td>1.54</td>
<td>Nil</td>
<td>1-0</td>
<td>Very bad</td>
</tr>
<tr>
<td>12.0</td>
<td>618</td>
<td>106</td>
<td>30</td>
<td>0.28</td>
<td>0.40</td>
<td>Nil</td>
<td>0-8</td>
<td>Polluted by trade waste</td>
</tr>
<tr>
<td>3.9</td>
<td>497</td>
<td>11</td>
<td>50</td>
<td>0.08</td>
<td>0.24</td>
<td>Nil</td>
<td>1-2</td>
<td>Fairly clean</td>
</tr>
<tr>
<td>4.0</td>
<td>356</td>
<td>14</td>
<td>50</td>
<td>0.24</td>
<td>0.20</td>
<td>Nil</td>
<td>1-2</td>
<td>Phenol—trace</td>
</tr>
<tr>
<td>16.0</td>
<td>407</td>
<td>5</td>
<td>200</td>
<td>0.98</td>
<td>Nil</td>
<td>2-0</td>
<td>Very bad</td>
<td></td>
</tr>
<tr>
<td>24.1</td>
<td>390</td>
<td>6</td>
<td>110</td>
<td>1.16</td>
<td>1.00</td>
<td>Nil</td>
<td>1-0</td>
<td>Phenol—trace</td>
</tr>
<tr>
<td>15.1</td>
<td>356</td>
<td>8</td>
<td>90</td>
<td>7.6</td>
<td>0.76</td>
<td>Nil</td>
<td>2-2</td>
<td>Very clean</td>
</tr>
<tr>
<td>10.0</td>
<td>340</td>
<td>11</td>
<td>50</td>
<td>7.6</td>
<td>0.84</td>
<td>Nil</td>
<td>2-0</td>
<td>Fairly clean</td>
</tr>
<tr>
<td>21.1</td>
<td>379</td>
<td>17</td>
<td>125</td>
<td>0.16</td>
<td>0.88</td>
<td>Nil</td>
<td>2-2</td>
<td>Very bad</td>
</tr>
<tr>
<td>12.2</td>
<td>402</td>
<td>12</td>
<td>125</td>
<td>0.64</td>
<td>0.72</td>
<td>Nil</td>
<td>1-2</td>
<td>Bad</td>
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<tr>
<td>13.3</td>
<td>412</td>
<td>14</td>
<td>120</td>
<td>0.60</td>
<td>0.72</td>
<td>Nil</td>
<td>1-2</td>
<td>Bad</td>
</tr>
<tr>
<td>17.3</td>
<td>507</td>
<td>19</td>
<td>120</td>
<td>0.88</td>
<td>0.72</td>
<td>Nil</td>
<td>1-6</td>
<td>Very bad</td>
</tr>
<tr>
<td>16.3</td>
<td>643</td>
<td>27</td>
<td>120</td>
<td>4.80</td>
<td>1.00</td>
<td>Nil</td>
<td>1-6</td>
<td>Very bad</td>
</tr>
<tr>
<td>20.9</td>
<td>592</td>
<td>32</td>
<td>110</td>
<td>3.92</td>
<td>1.00</td>
<td>Nil</td>
<td>2-2</td>
<td>Very bad</td>
</tr>
<tr>
<td>19.2</td>
<td>608</td>
<td>30</td>
<td>100</td>
<td>3.00</td>
<td>2.20</td>
<td>Nil</td>
<td>Nil</td>
<td>Big deterioration here due to waste from straw peeling</td>
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<tr>
<td>51.0</td>
<td>711</td>
<td>23</td>
<td>30</td>
<td>190</td>
<td>3.20</td>
<td>2.20</td>
<td>Nil</td>
<td>Very bad</td>
</tr>
<tr>
<td>49.0</td>
<td>706</td>
<td>24</td>
<td>10</td>
<td>190</td>
<td>6.80</td>
<td>2.00</td>
<td>Nil</td>
<td>Very bad</td>
</tr>
<tr>
<td>40.0</td>
<td>690</td>
<td>18</td>
<td>200</td>
<td>5.80</td>
<td>1.00</td>
<td>Nil</td>
<td>Nil</td>
<td>Very bad</td>
</tr>
<tr>
<td>50.6</td>
<td>726</td>
<td>20</td>
<td>190</td>
<td>5.40</td>
<td>1.40</td>
<td>Nil</td>
<td>Nil</td>
<td>Very bad</td>
</tr>
<tr>
<td>17.3</td>
<td>624</td>
<td>32</td>
<td>150</td>
<td>5.40</td>
<td>1.40</td>
<td>Nil</td>
<td>Nil</td>
<td>Very bad</td>
</tr>
</tbody>
</table>
### Table 120. Typical analyses of nitroglouous organic wastes

<table>
<thead>
<tr>
<th>Type of waste water</th>
<th>Appearance (settled)</th>
<th>pH</th>
<th>Transparency min sec through</th>
<th>Oxy. absorbed KMnO₄ unt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shakes</td>
<td>Settled</td>
</tr>
<tr>
<td>Piggery</td>
<td>Dark brown, opaque, foul odour; slight large dark brown sediment</td>
<td>6-8</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td>Brewery</td>
<td>Straw, very cloudy, much sediment (yeast cells)</td>
<td>5-2</td>
<td>4</td>
<td>51</td>
</tr>
<tr>
<td>Dairy (satisfactorily treated by alternating double filtration)</td>
<td>Colourless, clear trace of sediment</td>
<td>7-6</td>
<td>150</td>
<td>570</td>
</tr>
<tr>
<td>Dairy (poorly treated by alternating double filtration)</td>
<td>Almost colourless, very cloudy, much sediment</td>
<td>6-8</td>
<td>30</td>
<td>52</td>
</tr>
<tr>
<td>Pea vinining drainage</td>
<td>Greenish-straw, opaque; foul odour; large sediment</td>
<td>5-1</td>
<td>4</td>
<td>8</td>
</tr>
<tr>
<td>Vegetable preparation, washing (potatoes, etc.)</td>
<td>Yellow-brown, opaque, large dark brown sediment</td>
<td>9-6</td>
<td>10</td>
<td>12</td>
</tr>
<tr>
<td>Dehydrated vegetable mannior factor</td>
<td>Straw, turbid; very large brown sediment</td>
<td>4-5</td>
<td>5</td>
<td>20</td>
</tr>
</tbody>
</table>

### Table 121. Typical analyses of textile wastes

<table>
<thead>
<tr>
<th>Type of waste water</th>
<th>Appearance (settled)</th>
<th>pH</th>
<th>Transparency min sec through</th>
<th>Oxy. absorbed KMnO₄ unt.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Shakes</td>
<td>Settled</td>
</tr>
<tr>
<td>Cotton kier liquor</td>
<td>Deep brown, opaque</td>
<td>13-2</td>
<td>6</td>
<td>7</td>
</tr>
<tr>
<td>Viscose rayon</td>
<td>Colourless, cloudy, H₂S odour</td>
<td>2-0</td>
<td>187</td>
<td>220</td>
</tr>
<tr>
<td>Towel bleaching</td>
<td>Colourless, cloudy</td>
<td>3-9</td>
<td>50</td>
<td>100</td>
</tr>
<tr>
<td>Jute dyeing</td>
<td>Greenish-brown, opaque</td>
<td>6-6</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>Sulphide dyeing</td>
<td>Black, opaque</td>
<td>10-6</td>
<td>24</td>
<td>25</td>
</tr>
<tr>
<td>Calico printing</td>
<td>Deep grey-straw, very cloudy</td>
<td>11-2</td>
<td>25</td>
<td>38</td>
</tr>
<tr>
<td>Sponge cloth cleaning</td>
<td>Brown, opaque, oily odour</td>
<td>11-4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Screen printing and dying (cotton)</td>
<td>Greyish-brown, very cloudy, much sediment</td>
<td>6-4</td>
<td>20</td>
<td>35</td>
</tr>
<tr>
<td>Wooden piece goods scouring (cotton)</td>
<td>Greyish, opaque</td>
<td>11-0</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Dints, after treatment with acid and caustic</td>
<td>Colourless, fairly clear</td>
<td>6-0</td>
<td>190</td>
<td>420</td>
</tr>
</tbody>
</table>
### Table 120—cont.

<table>
<thead>
<tr>
<th>Total solids</th>
<th>Suspended matter</th>
<th>Alkalinity as CaCO₃</th>
<th>B.O.D. (1 day 20°C)</th>
<th>Ammoniacal N</th>
<th>Alumini-</th>
<th>Other</th>
<th>Methane</th>
<th>Biodegradability</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>Total</td>
<td>Min.</td>
<td>Vol.</td>
<td>Total</td>
<td>P.P.</td>
<td>M.O.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.250</td>
<td>2.527</td>
<td>42</td>
<td>80</td>
<td>157</td>
<td>—</td>
<td>—</td>
<td>1,275</td>
<td>20-0</td>
</tr>
<tr>
<td>811</td>
<td>1,037</td>
<td>455</td>
<td>344</td>
<td>779</td>
<td>—</td>
<td>—</td>
<td>4,550</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>26</td>
<td>—</td>
<td>—</td>
<td>90</td>
<td>0</td>
</tr>
<tr>
<td>704</td>
<td>1,370</td>
<td>20</td>
<td>120</td>
<td>140</td>
<td>—</td>
<td>—</td>
<td>330</td>
<td>432</td>
</tr>
<tr>
<td>8,150</td>
<td>27,250</td>
<td>34</td>
<td>104</td>
<td>138</td>
<td>—</td>
<td>—</td>
<td>12,880</td>
<td>—</td>
</tr>
<tr>
<td>1,050</td>
<td>4,400</td>
<td>32</td>
<td>383</td>
<td>415</td>
<td>180</td>
<td>650</td>
<td>5030</td>
<td>18-0</td>
</tr>
<tr>
<td>1,040</td>
<td>5,860</td>
<td>490</td>
<td>3,480</td>
<td>3,970</td>
<td>—</td>
<td>—</td>
<td>215</td>
<td>950</td>
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</table>

### Table 121—cont.

<table>
<thead>
<tr>
<th>Total solids</th>
<th>Suspended matter</th>
<th>Alkalinity as CaCO₃</th>
<th>B.O.D. (5 days 20°C)</th>
<th>Free chlorine</th>
<th>Oil</th>
</tr>
</thead>
<tbody>
<tr>
<td>Min.</td>
<td>Total</td>
<td>Min.</td>
<td>Vol.</td>
<td>Total</td>
<td>P.P.</td>
</tr>
<tr>
<td>12,240</td>
<td>19,800</td>
<td>5</td>
<td>8</td>
<td>13</td>
<td>6,000</td>
</tr>
<tr>
<td>4,500</td>
<td>5,840</td>
<td>46</td>
<td>30</td>
<td>78</td>
<td>1,375</td>
</tr>
<tr>
<td>1,318</td>
<td>2,052</td>
<td>46</td>
<td>59</td>
<td>105</td>
<td>180</td>
</tr>
<tr>
<td>802</td>
<td>2,113</td>
<td>174</td>
<td>289</td>
<td>463</td>
<td>—</td>
</tr>
<tr>
<td>2,308</td>
<td>3,173</td>
<td>32</td>
<td>61</td>
<td>93</td>
<td>200</td>
</tr>
<tr>
<td>1,019</td>
<td>2,020</td>
<td>31</td>
<td>101</td>
<td>132</td>
<td>500</td>
</tr>
<tr>
<td>2,990</td>
<td>5,429</td>
<td>134</td>
<td>819</td>
<td>953</td>
<td>425</td>
</tr>
<tr>
<td>1,800</td>
<td>2,882</td>
<td>968</td>
<td>1,355</td>
<td>2,253</td>
<td>—</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>16</td>
<td>179</td>
<td>195</td>
<td>441</td>
</tr>
<tr>
<td>—</td>
<td>—</td>
<td>7</td>
<td>24</td>
<td>31</td>
<td>Nil</td>
</tr>
</tbody>
</table>
### Table 122. Typical analyses of miscellaneous wastes

<table>
<thead>
<tr>
<th>Type of waste source</th>
<th>Appearance (briefly)</th>
<th>Reak (°C)</th>
<th>Brown (°C)</th>
<th>Oil absorbed (Kg/ha, net)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Salt works</td>
<td>Colourless, clear</td>
<td>8.9</td>
<td>&gt;800</td>
<td>0.6</td>
</tr>
<tr>
<td>Coal washing paper</td>
<td>Pale yellow, very black and cloudy</td>
<td>9.3</td>
<td>761</td>
<td>25</td>
</tr>
<tr>
<td>Coal washing (Steam)</td>
<td>Colourless, slightly cloudy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coal washing (Sulphur)</td>
<td>Colourless, slightly cloudy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Straw-bank paper</td>
<td>Dark brown, opaque</td>
<td>14.2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Paper pulp (pulp-making stage)</td>
<td>Colourless, slightly cloudy</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphuric acid liquor (wood pulp)</td>
<td>Reddish brown, cloudy</td>
<td>7.9</td>
<td>39</td>
<td>67</td>
</tr>
<tr>
<td>Coals washing paper</td>
<td>Light brown, cloudy</td>
<td>8.3</td>
<td>114</td>
<td>142</td>
</tr>
<tr>
<td>Galvanizing water (hot liquid)</td>
<td>Dark brown</td>
<td>8.8</td>
<td>640</td>
<td>695</td>
</tr>
<tr>
<td>Organic chemical manufacturer (Hot liquid)</td>
<td>Colourless, clear</td>
<td>7.6</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Organic chemical manufacturer (Hot liquid)</td>
<td>Colourless, clear, pharmonic odour</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lake fish manufacturers</td>
<td>Snow, steam, aromatic odour</td>
<td>12.5</td>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>Sand and gravel washing (hot water)</td>
<td>Yellow, very cloudy, very deep-smell odour</td>
<td>7.5</td>
<td>1</td>
<td>62</td>
</tr>
<tr>
<td>Sand and gravel washing (cold water)</td>
<td>Pale snow, rather cloudy, small odour</td>
<td>7.4</td>
<td>92</td>
<td>117</td>
</tr>
<tr>
<td>Potassium and boron compounds</td>
<td>Pale blue, very cloudy</td>
<td>8.8</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Lime-greening (sludge)</td>
<td>Pale green, very cloudy</td>
<td>8.0</td>
<td>31</td>
<td>31</td>
</tr>
<tr>
<td>Electroplating</td>
<td>Yellow, clear</td>
<td>8.8</td>
<td>612</td>
<td>612</td>
</tr>
</tbody>
</table>
### Table 122—cont.

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total solids</td>
<td>61,300</td>
</tr>
<tr>
<td>Suspended matter</td>
<td>2</td>
</tr>
<tr>
<td>Alkalinity (as CaCO₃)</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Assay test</th>
<th>Results in p.p.m.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulphate</td>
<td>5</td>
</tr>
<tr>
<td>Alkalinity</td>
<td>150</td>
</tr>
<tr>
<td>Chloride (as Cl)</td>
<td>5</td>
</tr>
<tr>
<td>Phosphates (as P₂O₅)</td>
<td>5</td>
</tr>
<tr>
<td>Ammonium (as N)</td>
<td>150</td>
</tr>
<tr>
<td>Other</td>
<td></td>
</tr>
</tbody>
</table>
### Table 123: Ministry of Health (now Ministry of Housing and Local Government) requirements for low-rate percolating filter plants.


<table>
<thead>
<tr>
<th>System</th>
<th>Tank capacity</th>
<th>Percolating filters* [see Note (1)]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Strong sewage</td>
</tr>
<tr>
<td>Detritus tank</td>
<td>2 or more equal to 2/3 D.W.F.</td>
<td>15</td>
</tr>
<tr>
<td>Septic tank†</td>
<td>2 or more, total equal to 1 day D.W.F.</td>
<td>45</td>
</tr>
<tr>
<td>Continuous settling tank</td>
<td>2 or more, total equal to 10-15 hours D.W.F.</td>
<td>45</td>
</tr>
<tr>
<td>Continuous chemical precipitation tank</td>
<td>2 or more, total equal to 8 hours D.W.F.</td>
<td>65</td>
</tr>
</tbody>
</table>

* Using coarse filter media (not to pass 1 in. sieve), or medium filter media (passing through 1 in. but not through 1/4 in. sieve).
† Only used for very small works.
D.W.F. = Dry Weather Flow in gallons per day of 24 hours.

**Notes on Table 123**

1. Minimum cubical contents (in yards) for treating 3 x D.W.F.
   - D.W.F. appropriate figure in table
2. Storm overflows. To operate at 6 x D.W.F. (this is now varied according to local circumstances; see Chapter 4, pages 72-6). No overflows at or near disposal works.
3. Screening. All sewage must be screened, including storm water.
4. Storm water. Sewage flows in excess of 3 x D.W.F. to be treated by settlement in two or more storm tanks (total capacity = 1 D.W.F.). No further treatment normally required. Land irrigation can be substituted for tanks.
5. Land. Contents of filters may be reduced to one-half where sufficient suitable land is available. In wet weather, 1 1/4 x D.W.F. should be treated in filters and the rest on land. Depending on the quality of the land, 3,000-30,000 gal. D.W.F. per acre per day of 24 hours.
6. Humus tanks. Where the effluent from percolating filters is not irrigated on land, humus tanks (capacity = 4 h D.W.F.) must be provided.
7. Strength of sewage. Can be based upon the McGowan strength figure (Chapter 12, page 419), or upon the n/80 acid permanganate 4 hours figure as suggested by Key (see Chapter 12, page 421).
8. Although the figures in the table are used as a basis for design, they are not necessarily rigidly followed but may be varied according to local circumstances.
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