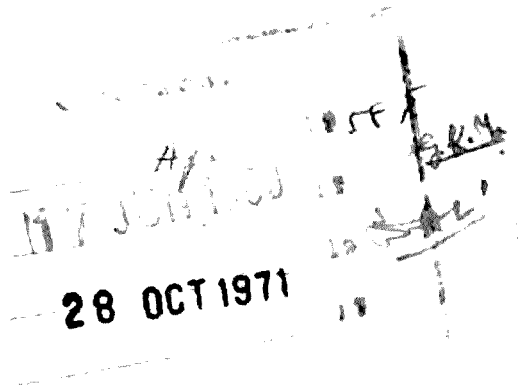
PROFESSOR JAYASHANKAR

TELANGANA STATE AGRICULTURAL UNIVERSITY




28 OCT 1971

399

AGRONOMY

A SERIES OF MONOGRAPHS

PREPARED UNDER THE AUSPICES OF THE
AMERICAN SOCIETY OF AGRONOMY

Volume IV

SOIL AND FERTILIZER PHOSPHORUS

in Crop Nutrition

Edited by
W. H. PIERRE and A. G. NORMAN

CONTRIBUTORS:

Z. A. ALTSCHULER
D. I. ARNON
C. A. BLACK
KATHARINE L. BUCK
G. J. CALLISTER
J. B. CATHCART
L. A. DEAN
L. E. ENSMINGER
M. FRIED
C. A. I. GORING
W. L. HILL
E. C. HOUSTON
V. IGNATIEFF
K. D. JACOB
L. T. KURTZ
V. E. MCKELVEY
A. MEHLICH
W. L. NELSON
S. R. OLSEN
F. W. PARKER
R. W. PEARSON
W. H. PIERRE
H. T. ROGERS
G. STANFORD
A. B. STEWART
R. W. SWANSON
E. TRUOG
J. H. WALTHALL
E. WINTERS

ANGRAU CENTRAL LIBRARY
Acc: No: 4790
Date: 27.2.86

G790
ANGRAU
Central Library
Rajendranagar

1953
ACADEMIC PRESS INC., PUBLISHERS
NEW YORK, N. Y.

PROCESSED

CHECKED 1997

G.790

COPYRIGHT, 1953 BY
ACADEMIC PRESS INC.
125 East 23rd Street
New York 10, N. Y.

All Rights Reserved

NO PART OF THIS BOOK MAY BE REPRODUCED IN ANY FORM, BY PHOTOSTAT, MICROFILM, OR ANY OTHER MEANS, WITHOUT WRITTEN PERMISSION FROM THE PUBLISHERS.

Library of Congress Catalog Card No. 53-11558

CHECKED

PRINTED IN THE UNITED STATES OF AMERICA

CONTRIBUTORS

Z. A. ALTSCHULER, *Mineralogist, U. S. Geological Survey, Department of the Interior, Washington, D. C.*

D. I. ARNON, *Professor of Plant Physiology, Department of Plant Nutrition, University of California, Berkeley, California*

C. A. BLACK, *Professor of Soils, Department of Agronomy, Iowa State College, Ames, Iowa*

KATHARINE L. BUCK, *Geologist, U. S. Geological Survey, Department of the Interior, Washington, D. C.*

G. J. CALLISTER, *Consultant to the Food and Agriculture Organization of the United Nations, Beamsville, Ontario, Canada*

J. B. CATHCART, *Geologist, U. S. Geological Survey, Plant City, Florida*

L. A. DEAN, *Senior Soil Scientist, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland*

L. E. ENSMINGER, *Associate Soil Chemist, Alabama Agricultural Experiment Station, Auburn, Alabama*

M. FRIED, *Soil Scientist, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland*

C. A. I. GORING, *Soil Scientist, Dow Chemical Company, Seal Beach, California*

W. L. HILL, *Principal Chemist, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland*

E. C. HOUSTON, *Chemical Engineer, Development Branch, Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama*

V. IGNATIEFF, *Deputy Technical Assistance Representative, North American Regional Office, Food and Agriculture Organization of the United Nations, Washington, D. C.*

ANGRAU
631.86
N53PIE
Acc No. G790

K. D. JACOB, *Head, Division of Fertilizer and Agricultural Chemicals, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland*

L. T. KURTZ, *Professor of Soil Fertility, Department of Agronomy, University of Illinois, Urbana, Illinois*

V. E. MCKELVEY, *Chief, Trace Elements Office, U. S. Geological Survey, Department of the Interior, Washington, D. C.*

A. MEHLICH, *Research Associate Professor of Agronomy, North Carolina State College, Raleigh, North Carolina*

W. L. NELSON, *in Charge, Soil Fertility Research, North Carolina State College, Raleigh, North Carolina*

S. R. OLSEN, *Senior Soil Scientist, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Fort Collins, Colorado*

F. W. PARKER, *Director of Soils Research, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Beltsville, Maryland*

R. W. PEARSON, *Senior Soil Scientist, Bureau of Plant Industry, Soils and Agricultural Engineering, U. S. Department of Agriculture, Auburn, Alabama*

W. H. PIERRE, *Head, Department of Agronomy, Iowa State College, Ames, Iowa*

H. T. ROGERS, *Head, Department of Agronomy and Soils, Alabama Polytechnic Institute, Auburn, Alabama*

G. STANFORD, *Associate Professor of Soils, Department of Agronomy, Iowa State College, Ames, Iowa*

A. B. STEWART, *Deputy Director, Macaulay Institute for Soil Research, Aberdeen, Scotland*

R. W. SWANSON, *Geologist, U. S. Geological Survey, Spokane, Washington*

E. TRUOG, *Chairman, Department of Soils, University of Wisconsin, Madison, Wisconsin*

J. H. WALTHALL, *Director, Division of Chemical Development, Tennessee Valley Authority, Wilson Dam, Alabama*

E. WINTERS, *Chief, Soils and Fertilizer Research Branch, Tennessee Valley Authority, Knoxville, Tennessee*

PREFACE

All aspects of the subject of phosphorus in relation to the growth of plants have attracted wide interest and attention in recent years. The activity of investigators has been such that the volume of knowledge has increased with great rapidity. The developments in this field have been followed closely in the United States by the National Phosphorus Research Work Group, which was appointed in 1948 by the National Soil and Fertilizer Research Committee, itself a body set up to survey, co-ordinate and review the research programs of the State Agricultural Experiment Stations and the relevant agencies of the U. S. Department of Agriculture. The Work Group in 1950 decided that it would be helpful to arrange for a Symposium at which the newer findings on soil and fertilizer phosphorus would be presented, and for a monograph covering the same field in greater detail, in order to make this information more widely available.

The membership of the Symposium Committee, which was responsible for the planning of the program, the selection of the speakers, and therefore, indirectly, for the structure of this book, was Roscoe E. Bell, Lyman Dean, Robert Gardner, C. Dale Hoover, Maurice H. Lockwood, A. R. Midgley, L. G. Monthey, W. L. Nelson, Eric Winters and W. H. Pierre, Chairman.

The Symposium was held at Urbana, Illinois, at the invitation of the University of Illinois, on August 26–28, 1952, under the sponsorship of the American Society of Agronomy, the Soil Science Society of America, and the National Soil and Fertilizer Research Committee.

This monograph was planned concurrently with the organization of the meetings. The authors of the respective chapters were the speakers at the Symposium; this volume is not, however, limited to the proceedings of the Symposium, nor do the chapters constitute a verbatim record of the presentations. Much additional material which could not be given orally because of time limitations is included herein with full citations of the original sources. For bibliographic reasons the undersigned have been designated as editors, though it will be apparent to any reader that the volume should properly be credited to the twenty-nine authors.

W. H. PIERRE, Ames, Iowa
A. G. NORMAN, Ann Arbor, Michigan

September 1953

INTRODUCTION

W. H. Pierre

Farmers and agricultural workers have long recognized the important role of soil and fertilizer phosphorus in crop production. Bone, the first important source of phosphorus fertilizer, was used in Great Britain as early as 1774. Its use increased steadily and about 100 years ago England was importing such large quantities of bone from the continent of Europe that Liebig, the noted German chemist, wrote with some alarm:

> "England is robbing all other countries of the condition of their fertility. Already in her eagerness for bones she has turned up the battlefields of Leipsig, of Waterloo, and of the Crimea; already from the catacombs of Sicily she has carried away the skeletons of many successive generations."

And in this country about forty years ago the noted conservationist C. R. Van Hise wrote:

> "The problem of the conservation of our phosphates is the most crucial, the most important, the most far-reaching with reference to the future of this nation of any of the problems of conservation."

Experience had shown that many soils in this country were deficient in phosphorus and that the use of phosphate fertilizers often materially increased crop yields. But little basic information was known forty years ago about such problems as the phosphorus status of different soils, the soil-plant relationships in the phosphorus nutrition of crops, and the comparative value of different phosphorus fertilizers. Neither was there knowledge of the large phosphate deposits later discovered in Florida and several of our western states.

Phosphate fertilizers formed the backbone of the fertilizer industry in the United States almost since superphosphate was first produced from South Carolina phosphate rock in 1868. But the total consumption in 1900 was only 246,000 tons (P_2O_5 equivalent). By 1920 it had reached a total of 640,000, and by 1940, 894,000 tons. The really large expansion in consumption, however, has come in the past fifteen years. In 1950, 2,434,000 tons (P_2O_5) were used in this

country and it has recently been estimated that the requirements during the next 10 to 15 years may increase to twice this amount.

It is probably not without significance that this rapid expansion in phosphorus fertilizer use follows and coincides with a marked expansion of research. During the 1935–1950 period, for example, a total of 673 major articles was published in the field covered in this monograph by research workers in the United States alone.* Two-hundred and forty of these related to studies of phosphorus fertilizer resources, the mining and engineering technology of fertilizer production, and the broad aspects of fertilizer consumption; whereas the remainder, or 433, dealt with research on soil phosphorus, soil-plant relationships and phosphorus fertilization.

There is little doubt that a large and valuable body of knowledge in this broad field has been developed in the past 25 years. Marked advances have been made in our understanding of the phosphorus reactions in plants and soils, of the phosphorus needs of different soils, and of the many problems related to the production and efficient utilization of soil and fertilizer phosphorus in crop production. This has resulted in part from our better understanding of soil chemistry and plant nutrition, the improvement of analytical methods, the refinement of design of field experiments and the greater use of statistical methods in interpreting experimental data.

As with most rapidly advancing fields, however, there is need occasionally to make a comprehensive and critical analysis or evaluation of the present state of our knowledge. This is especially true where the field of study is as broad and involves as many workers in different specialized areas or disciplines as does the field of soil and fertilizer phosphorus. Moreover, there is often a need for a panoramic as well as a keyhole view of the problems if gaps in the knowledge are to be uncovered and further progress realized. It was with these objectives in mind that the National Phosphorus Research Work Group planned the National Phosphorus Symposium and it was with these objectives that the authors of the various chapters of this volume undertook their task.

The wide scope of the problems relating to soil and fertilizer phosphorus in crop nutrition dealt with in this monograph is indicated by the titles of the various chapters. In general, the chapters can be considered under six major groupings, although these groupings are by no means mutually exclusive.

* Listed in the report of the National Phosphorus Work Group, entitled, "Summary of Phosphorus Research in the United States Relating to Soils and Fertilizers."

The first two chapters deal with the problems of soil-plant relationships. This includes the functions of phosphorus in plant nutrition, and the absorption of phosphorus by plants in relation to crop growth and composition and to available supplies in the soil.

The second group, which includes the next four chapters, deals particularly with soil phosphorus: the forms present in soils, their chemistry, reactions and transformations; and the availability of soil phosphorus to plants. It also includes a consideration of methods used in estimating the amounts of plant-available phosphorus found in different soils.

Chapters seven to ten, inclusive, deal more specifically with the value and use of phosphorus fertilizer, the comparative value of different carriers, the relation of soil management practices to the availability of native and applied phosphorus, and the laboratory evaluation of various phosphorus fertilizers.

The fourth group of problems, covered in chapters eleven and twelve, relates to our phosphorus fertilizer resources: the distribution, geology, and composition of the domestic deposits, and to the technological and economic factors influencing phosphorus fertilizer production in the United States.

In the last three chapters the more general problems of phosphorus fertilizer use are considered in relation to the phosphorus status of soils, crop requirements and potential fertilizer needs. The situation in the United States is first considered. Then, in view of the tremendous potential importance of phosphorus in world food production, a general analysis is presented in the final two chapters of phosphorus fertilizer needs in other parts of the world in relation to present fertilizer production and consumption.

CONTENTS

	Page
CONTRIBUTORS	v
INTRODUCTION	vii
PREFACE	ix
I. The Physiology and Biochemistry of Phosphorus in Green Plants	
DANIEL I. ARNON	
I. Introduction	1
II. The Absorption of Phosphorus by the Plant	1
III. Distribution of Phosphate in Tissues and Organs	9
IV. Phosphorus Deficiency Symptoms	12
V. Phosphorus Compounds in Plants	12
VI. The Role of Phosphorus in Energy Transfer Reactions in the Cell	24
VII. The Role of Phosphate in Carbohydrate Breakdown	28
VIII. The Role of Phosphate in Carbohydrate Synthesis	32
IX. Utilization of Phosphate Bond Energy	37
References	39
II. Soil-Plant Relationships in the Phosphorus Nutrition of Plants	
L. A. DEAN and MAURICE FRIED	
I. Introduction	43
II. Phosphorus Uptake from Soils	43
III. The Soil as a Supplier of Phosphorus	46
IV. The Phosphorus-Absorption Processes	52
References	56
III. Inorganic Phosphorus in Acid and Neutral Soils	
L. T. KURTZ	
I. Introduction	59
II. Forms and Amounts of Native Phosphorus in Soils	61
III. Reactions of Added Phosphates in Soils	67
IV. Crop Utilization of Different Forms of Phosphorus	78
V. Importance of Phosphate Fixation in Soil Fertility	79
References	80
IV. Inorganic Phosphorus in Alkaline and Calcareous Soils	
STERLING R. OLSEN	
I. Introduction	89
II. Definition of Alkaline and Calcareous Soils	89
III. The Forms of Soil Phosphorus	90
IV. The Properties of Calcium Phosphates	90
V. Reactions of Phosphate with Calcium Carbonate	94
VI. Reactions of Fertilizer Phosphorus with the Soil	97
VII. Some Properties of Residual Phosphate in Soils	106

Page

VIII. The Relationship of Surface Phosphate to Plant Available Phosphate in Soils ... 108
IX. Increase in Surface Phosphate from Residual Phosphate in Soils ... 115
X. Extraction of Residual Phosphates by Various Chemicals ... 117
References ... 118

V. Organic Phosphorus in Soils

C. A. Black and C. A. I. Goring

I. Determination ... 123
II. Amounts ... 131
III. Forms ... 132
IV. Transformations ... 136
V. Importance ... 141
References ... 144

VI. The Development, Evaluation, and Use of Soil Tests for Phosphorus Availability

W. L. Nelson, A. Mehlich, and Eric Winters

I. Introduction ... 153
II. Development of Soil Tests for Phosphorus Availability ... 155
III. Correlation of Soil Tests with Plant Growth ... 166
IV. Use of Soil Tests ... 177
References ... 183

VII. Comparative Efficiency of Various Phosphate Fertilizers

Howard T. Rogers, R. W. Pearson, and L. E. Ensminger

I. Introduction ... 189
II. Comparison of Phosphate Carriers Based on Crop Yields ... 190
III. Comparison of Materials Based on Absorption of Fertilizer Phosphorus, Using Tracer Technique ... 232
IV. Summary ... 233
References ... 236

VIII. Soil Management Practices in Relation to Phosphorus Availability and Use

George Stanford and W. H. Pierre

I. Introduction ... 243
II. Additions of Organic Materials ... 244
III. Rate, Time, and Frequency of Application ... 251
IV. Placement or Method of Application ... 257
V. Utilization of Subsoil Phosphorus ... 264
VI. Efficient Phosphate Use in Relation to Other Factors ... 270
VII. General Conclusions ... 272
References ... 273

IX. Liming in Relation to Availability of Native and Applied Phosphates

Emil Truog

I. Introduction ... 281
II. Field Experiments ... 283
III. Laboratory Tests ... 287
IV. Chemistry Involved ... 289
V. The Phosphorus Cycle ... 291
VI. Discussion ... 294
References ... 296

Page

X. Laboratory Evaluation of Phosphate Fertilizers

K. D. Jacob and W. L. Hill

I. Introduction 299
II. Phosphate Fertilizer Materials... 302
III. Methods of Evaluation in the Laboratory... 313
IV. Available Phosphorus as an Index of Nutrient Value.... 330
V. Bases for Guarantee and Quality Control of Fertilizer Phosphorus in Several Countries 337
References 340

XI. Domestic Phosphate Deposits

V. E. McKelvey, J. B. Cathcart, Z. S. Altschuler, R. W. Swanson, and Katharine L. Buck

I. Introduction 347
II. Principal Types of Phosphate Deposits.. 347
III. Distribution and Geology of Domestic Deposits 355
IV. Reserves 370
V. Acknowledgments 371
References 372

XII. Technical and Economic Factors Influencing Phosphate Fertilizer Production in the United States

J. H. Walthall and E. C. Houston

I. Introduction 377
II. Structure of the Industry 377
III. The Sulfur Problem..... 383
IV. Electric Furnace Process... 385
V. Nitric Phosphate Processes.. 387
VI. Uranium 392
VII. Particle Size, Caking, Drillability, and Granulation. 393
VIII. Western Phosphates 395
IX. Byproducts 396
References 399

XIII. Phosphorus Status and Requirements of Soils in the United States

F. W. Parker

I. Introduction 401
II. Phosphorus Status of Virgin Soils..... 402
III. Influence of Management on Phosphorus. 406
IV. Phosphorus Fertility Trends..... 413
V. Phosphorus Requirements 419
References 424

XIV. Factors Influencing Phosphate Usage in Great Britain

A. B. Stewart

I. Land Utilization and Fertilizer Consumption in Great Britain..... 427
II. Efficiency of Applied Phosphate..... 431
III. Conclusions 445
References 447

Page

XV. World Phosphorus Fertilizer Production, Consumption, and Potential Needs

V. IGNATIEFF and G. J. CALLISTER

I. Introduction 449
II. Phosphorus Fertilizer Production and Consumption: Prewar and Postwar Years (1936–1938 and 1946–1947; 1948–1949 and 1950–1951) 451
III. Potential Phosphorus Fertilizer Needs 458
IV. Acknowledgments 484
References 484

INDEX 487

CHAPTER I

The Physiology and Biochemistry of Phosphorus in Green Plants

DANIEL I. ARNON

I. Introduction

The purpose of this review is to survey the utilization of phosphorus by higher plants, including its absorption by the roots, movement and distribution within the plant, and participation in the metabolic reactions of the cell. Phosphorus has long been recognized as an essential constituent of all living organisms. In recent years, great advances have been made in the understanding of the physiological function of phosphorus in the conservation and transfer of energy in the metabolic reactions of living cells. Since this newer knowledge of the role of phosphorus in biological energy transformations has seldom found its way to agronomic literature, it will be necessary to introduce certain concepts and definitions which some readers will find superfluous. The present discussion will draw freely on the many excellent sources (Lipmann, 1941, 1951; Kalckar, 1941; Colowick, 1951; Kaplan, 1951; McElroy and Glass, 1951), to which the reader is referred for a full coverage of these important advances in biology. Only a selective treatment will be possible of the biochemical phases of the subject, which have already attained vast ramifications.

II. The Absorption of Phosphorus by the Plant

1. The Significance of Water-Soluble Phosphate in Soils

Phosphorus is absorbed by plants chiefly as the orthophosphate ion. A characteristic feature of phosphate absorption from soils is the ability of the plant to accumulate and maintain a high concentration of inorganic phosphate within its tissues, despite the low concentration of this ion in the soil solution. As shown by Pierre and Pohlman (1933) and others, the concentration of inorganic phosphate in the cell sap is frequently several thousand times higher than that in the displaced soil solution (Table I).

TABLE I

PHOSPHATE CONCENTRATION OF CELL SAP OF CORN AND OF DISPLACED SOIL SOLUTION[a]

Plant No.	In plant sap, p.p.m.			In soil solution (inorganic), p.p.m.	Concentration factor
	Inorganic	Organic	Total		
1	190	82	272	0.10	1900
2	171	99	270	0.31	552
3	154	50	204	0.06	2567
4	85	47	132	0.07	1214
5	149	44	193	0.08	1967
6	179	11	190	0.14	1278
7	154	22	176	0.09	1711
8	309	132	441	0.17	1818
9	259	104	363	0.09	2878

[a] After Pierre and Pohlman (1933).

An adequate phosphorus nutrition implies that the soil is able to supply this element to meet the requirements of the plant at all stages of its growth and development. It is obvious that, to insure an adequate total supply from the characteristically low concentration in the soil solution, repeated restoration of the water-soluble phosphate in soils is necessary. The water-soluble phosphate in the soil is in equilibrium with the phosphate in the solid phase. Given an adequate reservoir of phosphate in the solid phase, the speed with which equilibrium between the solid and liquid phase is attained can be taken as an indication of the supplying power of a soil for phosphorus. The attainment of this equilibrium is extremely rapid in most soils. The concentration of phosphate in the displaced solutions from soils of known acceptable productivity is often extremely low; it is, however, seldom below 0.05 p.p.m. and rarely above 10 p.p.m. (Teakle, 1928). In conventional nutrient solutions phosphate is usually supplied in concentrations of the order of a hundred or more parts per million and the concentration of inorganic phosphate in the plant sap (Table I) is usually from one hundred to several hundred parts per million (Tidmore, 1930; Pierre and Pohlman, 1933). It was legitimate, therefore, to inquire whether plants are able to absorb sufficient phosphate from the very low concentrations in the soil solution to meet the physiological requirements of rapid growth. A negative answer to this question would lead to the conclusion that the water-soluble phosphate of soils cannot be regarded as the principal source of supply, even if it were granted that a rapid equilibrium existed between the phosphate of the liquid and solid phase. An

auxiliary hypothesis, involving a mechanism for direct utilization of phosphate from the solid phase, would be required.

The adequacy of the displaced soil solution as a source of phosphate was studied by several investigators with the aid of the nutrient solution technique. The general objective was to determine the minimum phosphate concentration in a nutrient solution compatible with maximum plant growth. One procedure was to grow several representative species of crop plants in nutrient solutions at low phosphate concentrations. The concentrations were maintained constant within narrow limits by the use of large volumes of solutions in relation to the number of plants grown. Another procedure was to use flowing culture solutions. Although these investigations differed in the adequacy of the experimental techniques used, they were nevertheless concordant in establishing the fact that crop plants were able to absorb phosphate from extremely dilute solutions at rates sufficiently rapid to support maximal growth. Hoagland and Martin (1923) found that 0.70 p.p.m. of phosphate was sufficient to give favorable growth of barley; Parker and Pierre (1928) found that corn made maximum growth at a concentration of 0.10 p.p.m. of phosphate, if that concentration was maintained throughout the growing period; and Tidmore (1930) obtained maximum growth of corn, sorghum, and tomatoes at 0.5 p.p.m. of phosphate. It was thus made clear that the efficiency of phosphate absorption by higher plants from extremely dilute solutions is very high. It was demonstrated that the use of high concentrations of phosphate in conventional nutrient solutions is dictated by convenience of management rather than by physiological necessity. Nevertheless, the experimentally demonstrated adequacy of low concentrations of phosphate in the nutrient medium did not lead to the universal acceptance of the view that the soil solution is the sole direct source of phosphate for crop growth. It was pointed out by Parker (1927), and later by Parker and Pierre (1928), that the displaced solution of several productive soils had a phosphate concentration lower than those found necessary for maximum growth in nutrient solutions. Thus, Parker and Pierre (1928), who obtained maximum growth of corn at 0.10 p.p.m. phosphate in nutrient solutions, drew attention to several instances of productive soils whose displaced solutions contained only from 0.05 p.p.m. to a trace of phosphate. Likewise, Tidmore (1930) reported the results of an experiment in which plants grown in a soil having a displaced soil solution containing from 0.02 to 0.03 p.p.m. made better growth than those grown in culture solutions at 0.1 p.p.m. phosphate. The conclusion reached by these authors was that the water-soluble phosphate as found in the displaced soil solution could not by itself account for the phosphorus supply to crops. They in-

voked an additional mechanism, that of root soil contact, to explain phosphate absorption from soils. The nature of this mechanism was not specified, but it was envisaged as being distinct from absorption from the soil-solution phase.

In recent years, discussions of soil phosphorus accorded a prominent place to the anion-exchange concept (see review by Dean, 1949). It was found by several workers that phosphate ions fixed by soils can be displaced by such anions as hydroxyl, fluoride, arsenate, and silicate. The concept of anion exchange, unlike that of cation exchange, is confined to only one macronutrient, phosphate; nitrate and sulfate are not similarly adsorbed by the soil minerals. The mechanism of anion exchange in soils is beyond the scope of the present review, but as for the assessment of the possible contribution which anion exchange may make to phosphorus nutrition of crops, it is sufficient to state that it is one of the processes involved in the transfer of phosphorus between the solid and liquid phases of the soil. McAuliffe *et al.* (1947) studied with tracer techniques the exchange equilibrium of phosphate and hydroxyl ions between soil surfaces and solution. They found that only a small fraction of the phosphate presumed to be held as exchangeable anions was capable of rapid equilibration with the phosphate ions in the soil solution. On the other hand, the exchangeable cations on the soil minerals are highly mobile and attain rapid equilibrium with the cations in the liquid phase. Thus, there appear to be important differences between anion and cation exchange in soils. As opposed to the concept of cation exchange, the phenomenon of anion exchanges in soils does not seem to offer a basis for envisaging a contact exchange mechanism for the absorption of phosphate.

A survey of the work on phosphorus in the last twenty years brings to light no new concepts or facts which have advanced our understanding of the mechanism of phosphorus absorption by plants grown in soils. The physiological basis for understanding the absorption of phosphate ions by roots was established by the already cited work of Hoagland and Martin, Parker, Pierre, and Tidmore. It appears in retrospect that the interpretation of their work suffered from a misplacement of emphasis. Insufficient weight was given to their positive findings about the efficiency of higher plants in absorbing phosphate at rates compatible with maximum growth from extremely dilute nutrient solutions in which the concentration of phosphate was of the same order of magnitude as in *most* soil solutions. On the other hand, undue emphasis was placed on the few exceptions in which good crops were obtained in soils whose displaced solutions contained phosphate in concentrations lower than minimal in nutrient solutions. When it is recalled that these ex-

periments were carried out before the adoption of some of the present-day refinements in the nutrient solution technique of growing plants, it is indeed surprising that these exceptions were so few in number. A fresh appraisal of the evidence offers no compelling arguments against the view that the water-soluble phosphate is the source of phosphorus for plants grown under natural conditions in soils.

Fresh support for this conclusion is found in the recent work of Bingham (1951). Bingham investigated the correlation between water-soluble phosphate in soils and their supplying power for this nutrient as measured by pot tests with romaine lettuce and barley as indicator plants. These data were in turn compared with the response of the same soils to phosphate fertilization in the field and with the growth of the indicator plants in flowing nutrient solutions in which the phosphate concentration was kept constant. The data of Bingham cover an exceptionally wide range and provide an opportunity for an integrated analysis of the significance of water-soluble phosphate in soils by means of several independent criteria: chemical tests, pot culture experiments, field plot tests, and nutrient solution cultures.

Bingham adopted an aqueous equilibrium soil extract (soil:water = 1:10) as a standard test for essaying the phosphorus status of a soil. He applied this test to 300 California soils, which were then used for pot culture tests with romaine lettuce. For each soil, comparisons were made between pots fertilized with NPK and NK and the relative yields, $P_0\%$, were expressed as

$$P_0\% = \frac{\text{NK}}{\text{NKP}} \times 100$$

Bingham found that soils which had more than 1 p.p.m. PO_4 in the water extract test gave invariably high relative yields in both pot culture tests and field experiments and did not respond to phosphate fertilization (Fig. 1). Of special interest is a comparison of these results with those in the flowing nutrient solution. A recomputation on a relative yield basis of Bingham's data for lettuce grown in nutrient solutions is shown in Fig. 1. Excellent agreement is apparent between the relative yields in soil at a given level of water-soluble phosphate and the relative yields at the corresponding level of phosphate concentration in the nutrient solution (Fig. 1).

The data of Bingham provide additional support for the concept that phosphorus nutrition of plants grown in soils can be explained by the action of the water-soluble phosphate without the necessity of invoking any auxiliary mechanism. It will be noted that the new evidence, unlike that in the earlier experiments, is based, not on phosphate

levels of displaced nutrient solutions, but on phosphate concentrati in equilibrium water extracts of standardized, reproducible soil test

The Bingham water-soluble phosphate test was recently used Martin and Buchanan (1950) on 159 soils as a means of predict responses of grain crops to phosphate fertilization in the field. S which gave a phosphate test of less than 0.3 p.p.m. responded in

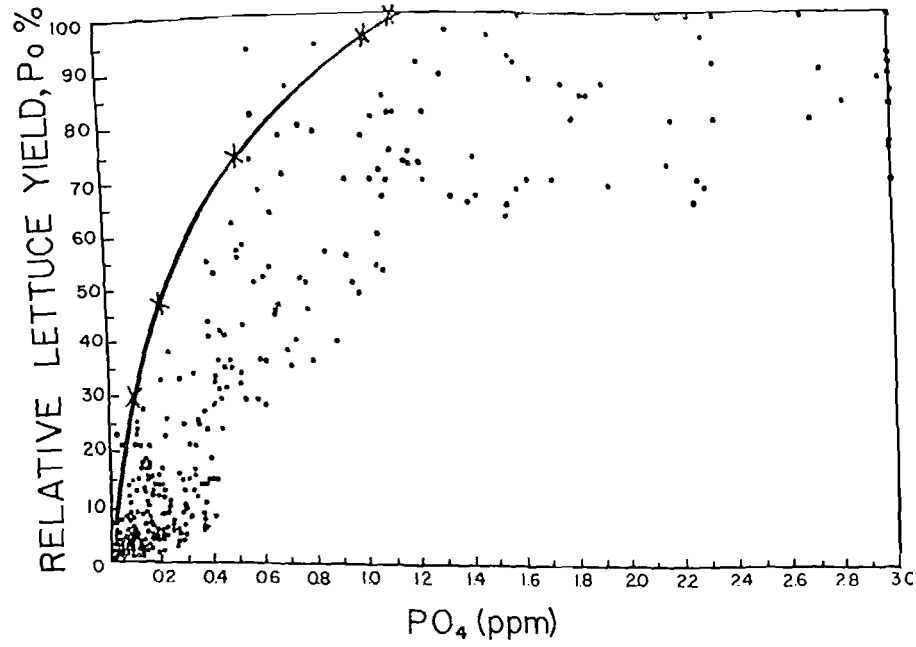


FIG. 1. Relative yields of lettuce in relation to phosphate concentration in nut solutions and water extracts of soils. Dots represent analyses of 1:10 water ext of individual soils; crosses represent phosphate concentration in the nutrient solu (after Bingham, 1951).

per cent of the cases to phosphate fertilization. Soils which gave a p phate test above 0.4 p.p.m. failed in 95 per cent of the cases to resp to phosphate fertilization in the field.

2. *Effect of Other Ions*

Phosphate is one of the three macronutrient anions absorbed plants. The absorption of phosphate would be expected, there (Hoagland, 1943), to be depressed by the presence in the nutr medium of high concentrations of rapidly absorbable anions and t increased by an increase in the concentration of rapidly absorb cations. An appropriate experimental design for testing these interi effects on phosphate absorption is provided by a comparison of monium and nitrate ions as the sole sources of nitrogen for pl

Fratzke, and Johnson, 1942). The results, shown in Fig. 2, are of special interest as far as absorption of phosphate at pH 9 is concerned. With all plants there was a sharp decline in phosphate absorption at that hydrogen ion concentration. The absorption of phosphate in the remainder of the pH range from 3 to 8 showed no distinct trend. The failure of plants to absorb phosphate at pH 9 in short-time absorption

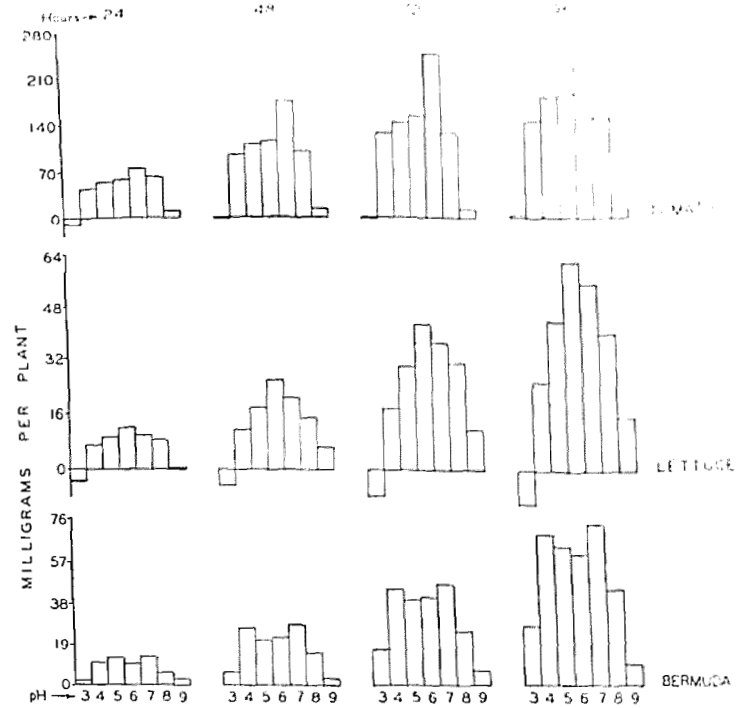


FIG. 2. Influence of pH of nutrient solution and time on the absorption of phosphate by tomato, lettuce, and Bermuda grass (Arnon, Fratzke, and Johnson, 1942).

experiments was concordant with the visual symptoms, strongly resembling phosphate deficiency, which were noted in the plants' growth at this pH for longer periods of time (Arnon and Johnson, 1942). Whatever other causes there may be for the failure of plants to grow at pH 9, the inability of plants to absorb phosphate at this pH would suffice to account for the deleterious effects on growth observed at this hydrogen ion concentration.

The failure of plants to absorb phosphate at pH 9 may perhaps be related to ionic form. Within the range of pH favorable for plant growth, phosphate exists in solution predominantly as the monovalent $H_2PO_4^-$ ion. At pH 9 the dominant ionic form of phosphate is the divalent $HPO_4^=$.

III. Distribution of Phosphate in Tissues and Organs

1. Upward Movement through the Plant

The advent of radioisotopes has made it possible to settle the long controversy about the path of movement within the plant of phosphate absorbed by the roots. Stout and Hoagland (1940) have shown by means of well-designed experiments with P^{32} that phosphate absorbed by the roots is distributed in the plant through the xylem. The upward movement of phosphate through the xylem, which is the main pathway for the distribution of newly absorbed phosphate, does not preclude secondary migrations or redistributions of phosphate in the plant through other channels. Biddulph (1951) has presented evidence for the downward migration of phosphate through the phloem and has discussed the significance of this mechanism to the phosphate economy of the plant.

2. Distribution as Governed by Physiological Need

Unlike certain inorganic nutrients such as calcium, phosphate has long been observed to be a mobile nutrient within the plant. Phosphate does not remain fixed in the cell or tissue in which it was originally deposited but is able to move from one site to another. There is abundant evidence for formulating a general rule which seems to govern the redistribution of phosphate within the plant. The requirement for phosphate is highest in the youngest cells or those characterized by a high rate of metabolic activity. When the external supply of phosphorus becomes limiting, there occurs a redistribution of the phosphorus already contained in the plant; phosphate is withdrawn from the older, metabolically less active cells and moves into the younger, metabolically more active cells. This phenomenon is readily demonstrated in the case of an induced phosphate deficiency. The symptoms of distress are first observable in the older, lower leaves. This circulation of phosphorus within the plant in accordance with a distinct "physiological priority" pattern has agronomic significance. Plants such as cereals, which are characterized by a determinate type of growth, do not require a continuous supply of phosphorus during their life cycle. The phosphorus absorbed in the early stages of growth and deposited in the vegetative tissues is redirected to the seed, at the stage of its active formation. Thus, Gericke (1924) found that the full requirements of wheat plants for phosphorus could be satisfied by supplying phosphate to the plants during only the first four weeks of their growth. Normal seed development occurred in a minus-phosphate nutrient medium on which the plants were placed subsequently. In plants such as the tomato, having

an indeterminate type of growth, characterized by a succession of new vegetative and fruit tissues, a somewhat different, but still consistent, pattern of phosphate distribution is observed. Arnon and Hoagland (1943) grew tomato plants for five weeks in complete nutrient solutions amply supplied with phosphate, until the emergence of the first flower. Plants were then selected for uniformity and were divided into two

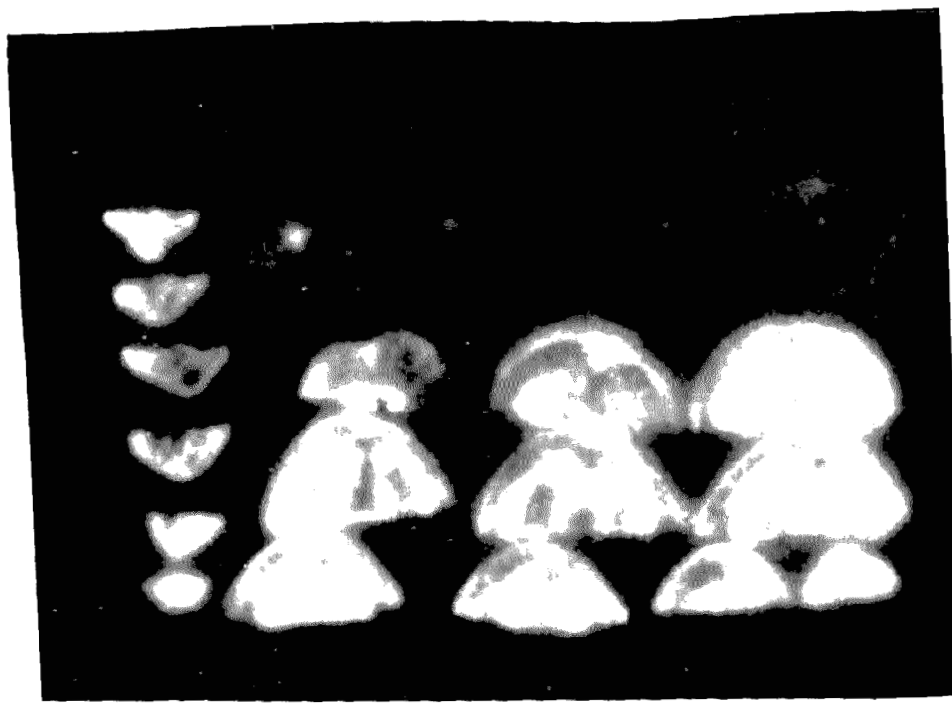


FIG. 3. Contact radioautograph of transverse section of tomato fruit at various stages of development. The fruits were removed at the same time after the introduction of radioactive phosphorus to the nutrient solution. Vertical column at the left represents sections of a small green fruit, the lower three horizontal columns are sections from a large green fruit, and the upper two horizontal columns are sections from a fully ripe fruit. The intensity of the images is in direct proportion to the concentration of radioactive phosphorus absorbed by the fruit (Arnon, Stout, and Sipos, 1940).

groups, which were placed in nutrient solutions with and without phosphate. Within the plus- and the minus-phosphate cultures, certain plants were allowed to form fruit while others were deflowered. It was found that in the minus-phosphate cultures the fruiting plants formed fruit at the expense of the phosphate absorbed by the vegetative tissues during the first five weeks. However, the total growth was severely restricted, being only one-fifth of that of the corresponding plants grown in the plus-phosphate solutions. The deflowered plants in the minus-

phosphate cultures made approximately twice the vegative growth of those allowed to fruit. When the supply was limiting, there was a redistribution of previously absorbed phosphate into new growing tissues in both the fruiting and the deflowered plants. In one case, the phosphate migrated to new fruit tissue, and, in the other, to new vegetative tissue.

This general relationship is illustrated in a more direct way by the use of radioactive phosphorus (Arnon, Stout, and Sipos, 1940). Tomato plants were grown up to the fruiting stage in complete nutrient solutions. The vines had green fruit in various stages of development. The plants were then divided into two groups which were placed into minus-phosphorus nutrient solutions. Radiophosphate was added to the nutrient solutions to give, in one case, a restricted (2.3 p.p.m.), and, in the other, a liberal (192.3 p.p.m.) phosphate supply. Experimental conditions other than phosphate supply were the same in the two cases. Plants were harvested from each group two and seven days after the addition of $P^{32}O_4$. It was found that the concentration of phosphorus increased with time in the green fruit, regardless of the external supply. The green fruit was divided on a fresh weight basis into three classes—small, medium, and large. The most active absorption of radiophosphate occurred in the youngest (small) fruit, i.e., the fruit which had the greatest capacity for growth and development. This was shown not only by radiochemical analyses but also by radioautography, as shown in Fig. 3. As for the distribution of newly absorbed phosphate in the

TABLE II

ABSORPTION OF $P^{32}O_4$ (P.P.M. DRY WT.) BY FRUIT-BEARING TOMATO PLANTS KEPT PRIOR TO TEST IN A COMPLETE NUTRIENT SOLUTION[a]

	Restricted external $P^{32}O_4$ supply, 2.3 p.p.m.		*Liberal external $P^{32}O_4$ supply, 192.3 p.p.m.*	
	Absorption time, days		*Absorption time, days*	
	2	*7*	*2*	*7*
Leaves				
Below fruit cluster	212	153	2,132[b]	10,266
Above fruit cluster	259	163	2,767	12,430
Green fruit				
Small (5 g.)	212	341	1,297	13,117
Medium (5–30 g.)	132	161	799	6,521
Large (30 g.)	63	80	404	3,107

[a] After Arnon, Stout, and Sipos (1940).

[b] Only first three figures are regarded as significant.

leaves, significant differences were observed between the plants at the two levels of phosphate supply. As shown in Table II, given a liberal phosphate supply, both the leaves and the fruit showed a gain in phosphorus. With the restricted supply, phosphate was withdrawn from the leaves and transported into the fruit. Under these conditions, the development of the fruit proceeded at the expense of the vegetative organs.

IV. Phosphorus Deficiency Symptoms

As with other nutrients, some of the symptoms associated with phosphorus deficiency are not specific. The growth of both shoots and roots is greatly reduced and the growth habit is often upright and spindly; premature defoliation beginning with the older leaves is common; lateral shoots are few in number and lateral buds may die or remain dormant; blossoming is greatly reduced with consequent poor yields of grain and fruits; the opening of buds, leaves, and blossoms in the spring is delayed. One of the most common diagnostic aids in identifying phosphorus deficiency is the color of the foliage. In many plants phosphorus deficiency is recognized by the purple, and sometimes bronze, tinge of the leaves, which are generally characterized by a dull, bluish green color with purple or brown spots. Leaf margins may show brown scorching. Although the purple tinge of the foliage is characteristic, it is not an infallible guide to the identification of phosphorus deficiency. A modification of the anthocyanin pigment metabolism by other causes sometimes produces similar effects.

V. Phosphorus Compounds in Plants

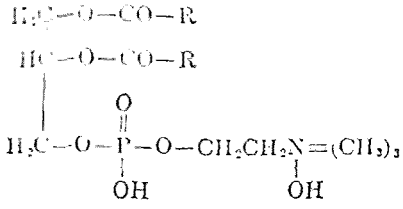
1. Inorganic Phosphate

Phosphate, unlike the other two macronutrient anions, nitrate and sulfate, is not reduced in the plant. It is found in plant as well as in animal tissue as a phosphate radical, never as phosphite or elemental phosphorus. Phosphorus exists in plants as both the inorganic phosphate ion and in combination with organic compounds, the most important of which will be discussed below. Inorganic phosphate occurs in relatively large amounts in the vacuolar sap (Table I). Phosphate is a component of the buffer system of plants. The physiological significance of the inorganic phosphate in cellular metabolism will be discussed in subsequent sections of this article.

2. Phospholipids

Among the organic compounds of phosphorus, the phospholipids or lipids containing phosphorus have long been known as components of

all living cells. The phospholipids are distinguished from other lipids in being insoluble in acetone. Three groups of phospholipids are known —lecithins, cephalins, and sphingomyelins. Lecithins are composed of glycerol, fatty acids, phosphoric acid, and the quaternary base, choline.

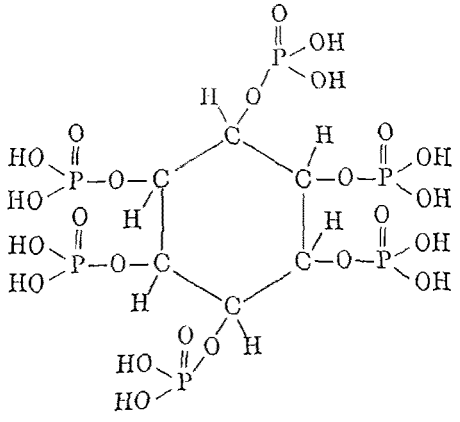


α-Lecithin

Cephalins are similar to lecithins, with the exception that the place of choline in the molecule is taken by cholamine. Cephalins containing the amino acid, serine, in place of cholamine have recently been discovered. Sphingomyelins are composed of a fatty acid, phosphoric acid, choline, and a complex amino alcohol, sphingosine. They do not contain glycerol.

3. *Phytin*

A form of organic phosphate of special interest to plants is phytic acid. Phytic acid is the hexaphosphoric acid ester of inositol or hexahydroxycyclohexane. In the plant phytic acid is usually present in the



Phytic acid

form of calcium and magnesium salts known as phytin. Phytin serves as the storage form of phosphate in seeds which contain very little inorganic phosphate. On germination, phosphate from phytin becomes available for the phosphorylation reactions in the metabolism of the seedling (Albaum and Umbreit, 1943). Phytin has also been found in peanuts, peas, potatoes, and carrots (McCance and Widdowson, 1935).

A. *Phosphorylated Sugars*

The oxidation of hexoses in respiration and in reverse their formation in photosynthesis has long been represented by the familiar equation:

$$C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6H_2O$$

This equation as written shows no participation of phosphate in the reaction. Yet, one of the great advances of the present century in the understanding of the chemistry of life phenomena has been the demonstration and elucidation of the role of phosphorus in carbohydrate metabolism. The story began in 1905, when Harden and Young found that in the fermentation of glucose by yeast juice, inorganic phosphate was being consumed. Soon thereafter specific sugar phosphate esters were identified, and from the work of many investigators gradually developed an understanding of the carbohydrate transformations in living cells. It was found that free sugars are not used directly in cellular metabolism. They are first converted into phosphate esters which undergo a series of stepwise transformations. The reaction for the oxidation of glucose, as written above, was shown to be an overall summation of many distinct reactions, each catalyzed by an individual enzyme.

It was found that the metabolism of glucose in all living organisms included an anaerobic phase, referred to as the glycolytic cycle, during which one molecule of glucose is split and dehydrogenated to two molecules of pyruvate. (The strict definition of the glycolytic cycle or glycolysis includes also the reduction of pyruvate to lactate.) Pyruvate is then further oxidized to carbon dioxide and water as in the case of aerobic cells or, as in yeast fermentation, it is transformed to alcohol and CO_2. The transformation of sugar to pyruvate is shown in Fig. 4. Each of the steps involves a phosphorylated compound and each transformation is catalyzed by a specific enzyme. The evidence for the occurrence in green plants of these phosphorylated intermediates and their corresponding enzymes will be found elsewhere (Albaum, 1952; Stumpf, 1952a).

The glycolytic cycle, also known as the Embden-Meyerhof scheme, is recognized as the principal initial pathway of carbohydrate metabolism. The main features of the glycolytic cycle, as represented by the series of reactions in Fig. 4, are that the hexose molecule is doubly phosphorylated by reactions 3 and 5, split into two trioses by the aldolase reaction 6, and the triose molecule is oxidized by reaction 8 with a simultaneous uptake of inorganic phosphate. The resulting diphos-

phoglyceric acid transfers first one phosphate group (9) and then, after undergoing dehydration by the enolase reaction 11, transfers the other phosphate group (12) to adenosine diphosphate (see Section V. 6).

As already stated, the series of reactions shown in Fig. 4 can take place under anaerobic conditions, but it has been generally accepted

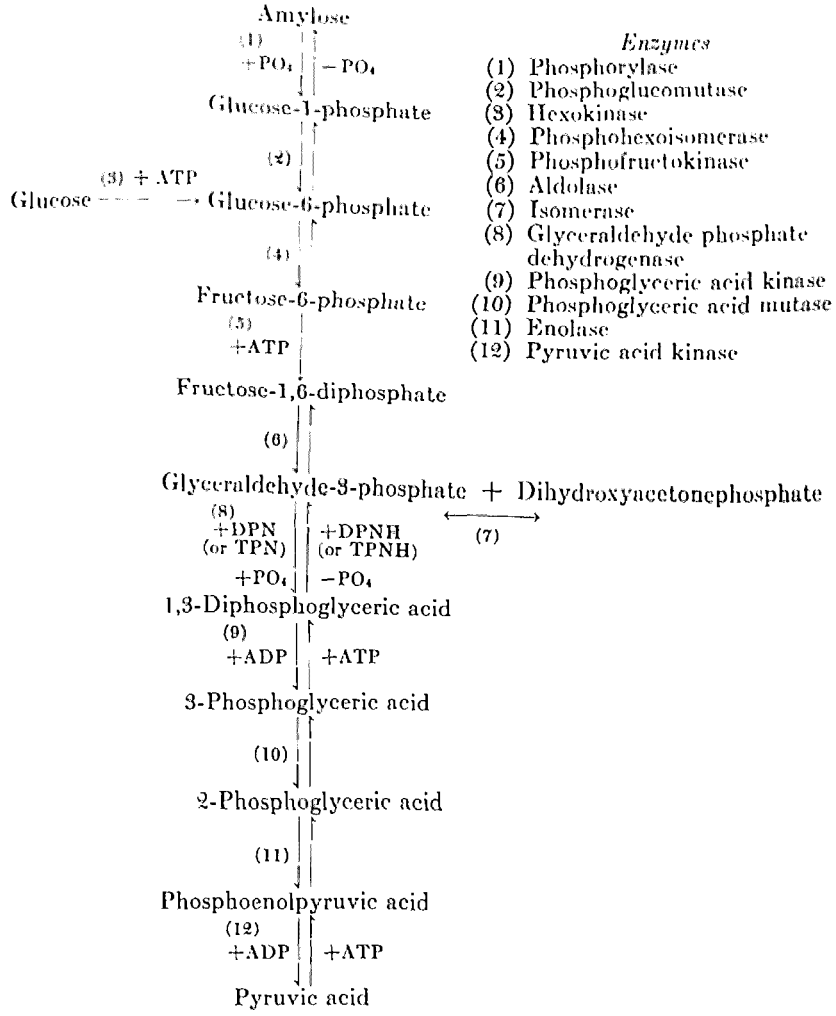
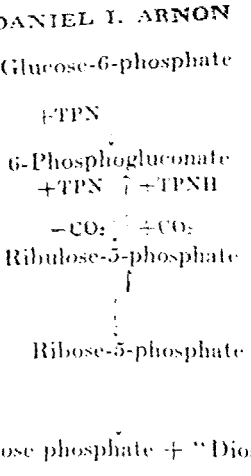
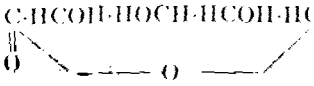


FIG. 4. The glycolytic cycle.

that, in aerobic metabolism as well, the oxidation of glucose to carbon dioxide and water involves first the transformation of glucose to pyruvate by the anaerobic glycolytic pathway. There is increasing evidence, however, that under aerobic conditions an alternative pathway for the breakdown of glucose-6-phosphate, as shown below, may be of considerable importance (Horecker, 1951; Cohen, 1951).



This scheme involves first an oxidation of glucose-6-phosphate to 6-phosphoglucolactone (Lipmann, 1951)

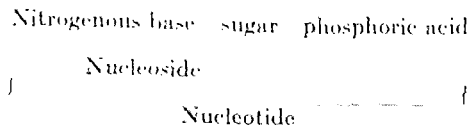


by a TPN-specific dehydrogenase. The 6-phosphogluconic acid that is formed by the hydrolysis of the lactone is oxidatively decarboxylated by another TPN-dependent enzyme to a keto pentose sugar, ribulose-5-phosphate. The ribulose-5-phosphate is slowly converted by a pentose phosphate isomerase into ribose-5-phosphate. The pentose phosphate is cleaved into a triose phosphate and an as yet unidentified two-carbon fragment designated as a "diose." The triose phosphate is then available for hexose synthesis by the aldolase reaction (Fig. 4). The full significance of the oxidative pathway for glucose degradation cannot be determined at this time. It is clear that it provides a mechanism for pentose formation, but it may have other functions in carbohydrate metabolism. There are indications that this oxidative pathway is operative in green plants.

5. *Nucleoproteins and nucleic acid*

Nucleoproteins constitute a group of organic phosphorus compounds of special significance to all living cells. As their name implies, these compounds are especially associated with cell nuclei. Nucleoproteins are conjugated proteins, that is, combinations of simple proteins, generally of basic character, with nucleic acid. Nucleic acid is a complex of purine and pyrimidine bases, sugar, and phosphoric acid. Nucleoproteins are most intimately concerned with cellular organization, function, and reproduction. They constitute a large part of the nucleus and are also present in the cytoplasm. They are constituents of chromosomes and genes and are thus intimately concerned in the transmission of

hereditary characteristics. Tobacco, cucumber, and other plant viruses have been isolated as crystalline nucleoproteins. Two types of nucleic acid are generally recognized, one derived from yeast, and one from the calf thymus gland. When nucleic acid is treated with dilute alkali, it is split into components, made up of one molecule each of phosphoric acid, pentose sugar, and a nitrogenous base. These components are called nucleotides and are differentiated by the different bases which they may contain. A molecule of nucleic acid is made up of many nucleotide units, just as a molecule of protein is made up of many amino acids. The phosphoric acid of nucleotides is present in a terminal ester linkage, and it can be split off by enzymatic hydrolysis with nucleotidase (a phosphatase), leaving a compound called nucleoside.



The sugar present in yeast nucleic acid has been identified as D-ribose, and that in thymus nucleic acid as D-2-desoxyribose. The purine bases of yeast and thymus nucleic acid are guanine and adenine. The pyrimidine bases of yeast nucleic acid are cytosine and uracil and those of thymus nucleic acid are cytosine and thymine.

The nomenclature of nucleotide and nucleosides will be briefly reviewed here, since it is important for the discussion of the metabolic role of phosphate that is to follow. These compounds are designated according to the specific purine or pyrimidine base which they contain. Thus,

Adenine nucleotide (Adenine + Sugar + Phosphoric acid) = Adenylic acid
Cytosine nucleotide (Cytosine + Sugar + Phosphoric acid) = Cytidylic acid

The corresponding nucleosides are

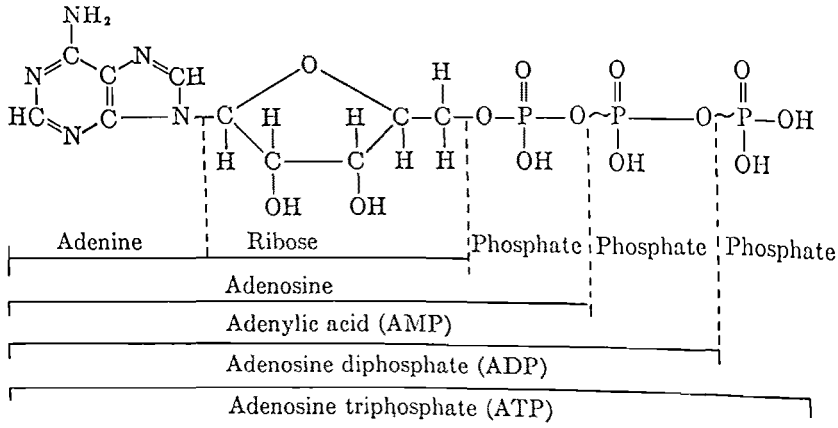
Adenine nucleoside (Adenine + Sugar) = Adenosine
Cytosine nucleoside (Cytosine + Sugar) = Cytidine

Since the sugar of a nucleotide or a nucleoside may be either ribose or desoxyribose, the corresponding designations become ribonucleotide or desoxyribonucleotide and ribonucleoside and desoxyribonucleoside or, for the nucleic acid as a whole, ribonucleic and desoxyribonucleic acid. It was believed at one time that plant nucleic acid was of the yeast or ribonucleotide type and that animal nucleic acid was of the thymus or desoxyribonucleotide type. At the present time, it is recognized that both types of nucleic acid occur in the nucleoproteins of plants and animals (Albaum, 1952). It appears, however, that desoxyribonucleic

acid occurs only in the nucleus, whereas ribonucleic acid is found in both nucleus and cytoplasm. Nucleoproteins of the desoxyribonucleic acid type seem to be localized in the chromosomes.

6. The Adenylic Acid System

The adenine nucleotides occupy a key position in the storage and transfer of energy in the metabolic reactions of living cells. They perform this function by accepting phosphate groups from metabolic intermediates, binding them in a pyrophosphate linkage (P—O—P), and in turn transferring them, by reactions termed phosphorylations, to other compounds involved in intermediary metabolism. The phosphate group passes from the organic "donor" to the organic "acceptor" molecule without going through the stage of inorganic phosphate. The adenine nucleotides concerned in the transphosphorylation reactions are jointly referred to as the adenylic acid system. Adenylic acid itself is a ribonucleotide. Its one phosphate group is linked to ribose by an ester linkage and it is not detached in the transphosphorylation reactions. Adenylic acid combines in a pyrophosphate linkage with two molecules of phosphoric acid to form a triphosphate. Since adenylic acid is, according to the nomenclature discussed above, the nucleoside adenosine, linked to one phosphate group, it is commonly designated adenosine monophosphate (AMP). The pyrophosphate compound which contains three phosphate groups is termed adenosine triphosphate (ATP). The formulas of ATP and related compounds are given below:



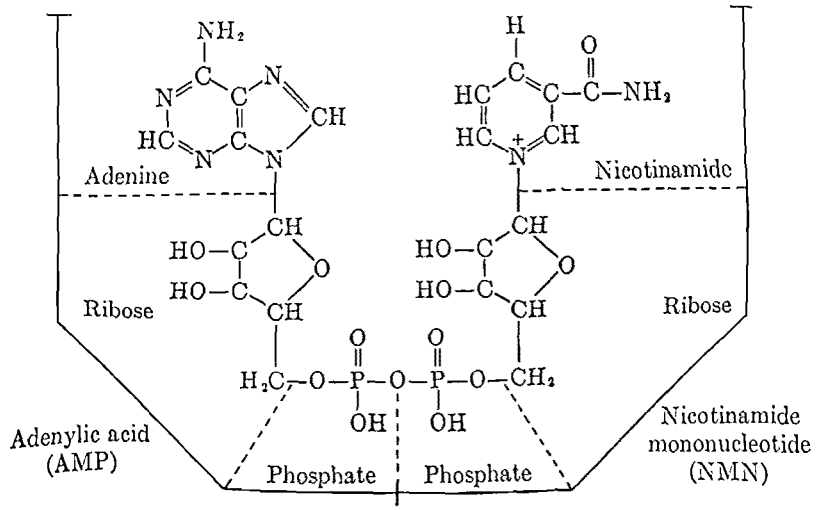
The pyrophosphate (P—O—P) bond of the two end phosphate groups of ATP is known as a "high-energy bond" (~ ph), signifying that when it is broken (as on hydrolysis of the terminal phosphate group) there is a large release of energy, about 12,000 calories. In phosphorylation reactions involving the adenylic acid system, it appears that only

ATP serves as the phosphate donor. ATP transfers its terminal phosphate group to a suitable phosphate acceptor. In these reactions ATP, having lost one phosphate group, becomes adenosine diphosphate (ADP). ADP serves in turn as a phosphate acceptor in metabolic reactions in which a high-energy phosphate bond has been generated. Upon accepting a phosphate group ADP is converted into ATP. ADP does not serve directly as a phosphate donor, nor can AMP serve as a phosphate acceptor (Colowick, 1951). However, a widely distributed enzyme myokinase or adenylkinase, which was first found in animal tissues, catalyzes the reversible reaction:

$$2ADP \rightleftarrows ATP + AMP$$

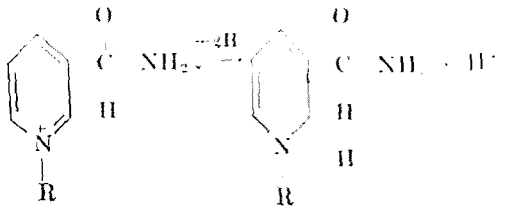
7. *Pyridine Nucleotides*

In the enzymatically catalyzed oxidations and reductions of biological substrates, the essential function of electron or hydrogen transfer is generally not associated with the protein moiety (apoenzyme) of the enzyme system, but rather with a prosthetic or active group which can be either a metal or a coenzyme. Two of the most important of these coenzymes are the pyridine nucleotides: diphosphopyridine nucleotide (DPN), also known as coenzyme I; and triphosphopyridine nucleotide (TPN), also known as coenzyme II. TPN has the same structure as DPN except that, in addition to the two phosphate groups in the pyrophosphate linkage, it has a third phosphate group attached to the ribose of the adenylic acid moiety of the DPN molecule (Kornberg, 1951). The structure of DPN is given below.



DIPHOSPHOPYRIDINE NUCLEOTIDE (DPN)

DPN and TPN serve, in association with enzymes known as dehydrogenases, as hydrogen or electron carriers by undergoing reversible oxidations and reductions in the nicotinamide part of the molecule as represented below. (R signifies the remainder of the molecule.)



Oxidized DPN Reduced DPN (DPNH)

The oxidation-reduction of DPN and TPN does not involve the phosphate groups of the molecule. Nevertheless, it is well established that certain dehydrogenases are specific for DPN and others for TPN. This suggests that the phosphate groups may play a role in the attachment of the coenzymes either to the substrate or to the apoenzyme.

DPN and TPN provide a biochemical function for the vitamin nicotinamide (niacin) and demonstrate its essentiality in specific metabolic reactions in both plants and animals. DPN can be reversibly converted into TPN (McElroy and Glass, 1951). In yeast and in animal tissues DPN occurs in much greater quantities than TPN (Schlenk, 1951). The reverse seems to be true, however, in green leaves (Whatley, 1951).

DPN is required by many dehydrogenases which have been studied in detail in yeast, animal tissues, and bacteria. As examples of DPN-linked enzymes of plants, the alcohol and glyceraldehyde phosphate dehydrogenase (Stumpf, 1952a) of pea seeds can be cited. Isocitric dehydrogenase is an example of a TPN-specific enzyme found in green leaves (Whatley, 1951).

The general mode of action of DPN and TPN in oxidation-reduction can be represented as follows:

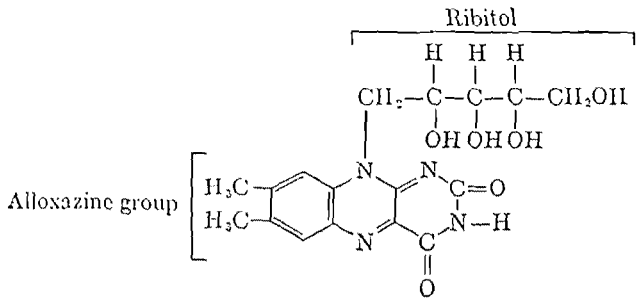
$$A{\cdot}H_2 + \underset{\text{(or TPN)}}{DPN} \rightleftharpoons A + \underset{\text{(or TPNH)}}{DPNH} + H^+$$

where A is the metabolic substrate.

8. Flavin Nucleotides

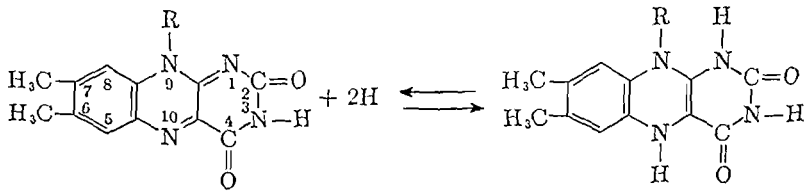
In 1932, Banga and Szent-Györgyi obtained a yellow substance from heart muscle and observed that the yellow color disappeared on reduction and reappeared on oxidation. They suggested that the yellow substance, which they called "cytoflav," may be involved in cellular

respiration. In the same year, Warburg and Christian prepared a yellow enzyme from brewer's yeast. The enzyme was shown to be a compound consisting of a colorless protein linked to a yellow component serving as the prosthetic or active group of the enzyme (Theorell, 1937). The yellow component was found to be riboflavin phosphate, consisting of a phosphate group joined to riboflavin, a yellow substance, synonymous with vitamin B_2 and widely distributed in plant and animals cells and in such foods as milk. Riboflavin is not derived from the ribose sugar, as the name would suggest. Rather the pentahydric sugar alcohol *d*-ribitol is linked with the nitrogenous base 6-7-dimethyl-isoalloxine in the following manner:



Riboflavin

The yellow enzyme can be reconstituted after splitting by combining the riboflavin phosphate (flavin mononucleotide, FMN) with the protein. Enzymes of this type have been designated flavoproteins. Flavoprotein enzymes play an important part in the oxidation-reduction reactions of the cell by serving as intermediaries in the transport of hydrogens or electrons. The prosthetic group which is involved in the hydrogen transfer is the alloxazine group of the riboflavin, according to the following equation:



Alloxazine group oxidized form

Alloxazine group reduced form

A number of flavoproteins have been isolated from natural sources, including green plants. Most of the flavoprotein enzymes were found to contain as a prosthetic group, not FMN, but flavin adenine dinucleotide

(FAD). FAD can be synthesized, with the aid of an appropriate enzyme, from FMN and ATP, according to the following reaction (Kornberg, 1951):

Flavin—ribitol-P + P~P + P—ribose—adenine
FMN ATP
Flavin—ribitol—P—P—ribose—adenine + P~P
FAD Pyrophosphate

The flavoproteins are reduced by accepting hydrogen from two sources: (1) reduced coenzymes I and II (DPNH and TPNH), or (2) other substrates or hydrogen donors such as glucose, aldehydes, and amino acids. The reactions can be represented as follows:

(1) DPNH + H^+ + FAD → DPN$^+$ + FADH_2
(or TPNH) (or TPN$^+$)

(2) AH_2 + FAD → FADH_2 + A
(substrate)

The reduced flavoprotein is reoxidized by oxygen either directly or indirectly with the aid of the cytochrome system.

The structural relations of the nucleotides discussed so far are given in the following schematic summary:

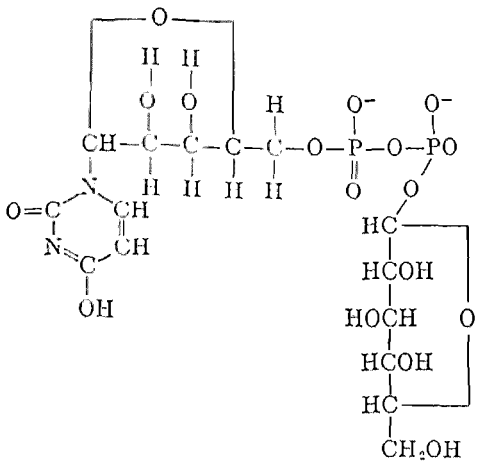
		PO_4
TPN	Nicotinamide—ribose—	PO_4—PO_4—ribose—adenine
DPN	Nicotinamide—ribose—	PO_4—PO_4—ribose—adenine
FAD	Flavin— ribitol—	PO_4—PO_4—ribose—adenine
FMN	Flavin— ribitol—	PO_4
ATP		PO_4—PO_4—PO_4—ribose—adenine
ADP		PO_4—PO_4—ribose—adenine
AMP		PO_4—ribose—adenine

9. Other phosphorus compounds as prosthetic groups of enzymes

In addition to those discussed above, other phosphorus compounds were found to serve as prosthetic groups of enzymes derived from yeast, bacteria, animal tissues, and in some cases higher plants. Although our knowledge of their importance in the metabolism of green plants is as yet either limited or based merely on analogy with other organisms, their full importance in plant physiology may be revealed at any time.

A case in point is uridine diphosphate glucose (UDPG). Uridine itself is uracyl-ribose nucleoside. UDPG has recently been isolated from yeast and bacteria and was found to be the coenzyme responsible for the reversible conversion of glucose-1-phosphate, into galactose-1-phos-

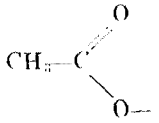
phate (Leloir, 1951). The following structure has been assigned to UDPG.



Uridine diphosphate glucose (UDPG)

Recent as is the discovery of UDPG, there is already evidence that UDPG and uridine diphosphogalactose are among the early products of photosynthesis (Buchanan *et al.*, 1952). These authors believe that uridine diphosphate compounds are involved in the synthesis of polysaccharides in the plant and particularly in sucrose synthesis.

Coenzyme A is a new coenzyme involved in the transfer of acetyl groups



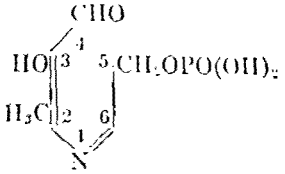
or other acyl groups in many metabolic reactions of microorganisms, animals, and plants, the carrier of the acetyl groups being acetyl—coenzyme A. The activation of acetate requires coenzyme A in addition to ATP. Coenzyme A contains adenosine-5-phosphate, two additional phosphate groups, panthothenic acid, and a sulfur-containing group. An enzyme recently discovered in bacteria, called phosphotransacetylase, allows acetyl phosphate to serve as an acetyl donor, according to the reaction:

$$\text{Acetyl} \sim \text{P} + \text{CoA} \rightleftharpoons \text{Acetyl—CoA} + \text{PO}_4$$

The acetyl group when activated in this manner can be transferred to an acetyl acceptor, such as amine, acetate, and oxalacetate. The acetyl group will condense either by its methyl group, as in citrate

synthesis, or by its carboxyl group, as in the synthesis of acetyl sulfonamides. It is also probable that, in the reaction from right to left, the enzyme catalyzes the formation of acetyl phosphate from pyruvate, acetaldehyde, citrate, and possibly also from acetoacetate and butyrate.

Pyridoxal phosphate has recently been shown to be a coenzyme of amino acid decarboxylases and certain transaminating enzymes. The position of the phosphate group in the molecule is not entirely certain, but the present evidence favors the structure given below.



Thiamin pyrophosphate, also known as cocarboxylase or diphosphothiamine, has long been shown to act as a coenzyme for both nonoxidative and oxidative decarboxylations of pyruvate.

VI. The Role of Phosphorus in Energy Transfer Reactions in the Cell

The maintenance of life processes requires energy. Plants and animals derive the necessary energy from the oxidation of foodstuffs. These, in the final analysis, make available to the living cell the energy of sunlight, which has been converted and stored in the form of chemical energy during photosynthesis. Green plants share with heterotrophic organisms the need for suitable mechanisms for rendering the chemical energy stored in foods available for cellular metabolism. Green plants occupy, however, a unique position in the living world in possessing additional mechanisms for the direct capture of the energy of sunlight and its conversion into chemical energy.

A central problem in energy transformations in the living cell is that of energy transfer. Energy, whether liberated as in respiration or captured as in photosynthesis, must be bound and transported from one site to another in the living cell if it is not to become dissipated in the form of heat. At least two mechanisms are known for accomplishing these energy transfers within the cell: the formation of high-energy phosphate bonds and the transfer of electrons (or hydrogen) by means of the pyridine nucleotides, DPN and TPN.

1. The Concept of High-Energy Phosphate Bonds

The organic phosphate compounds in living cells can be divided into two groups: one in which the phosphate group is bound to its carrier by a "strong linkage" and the other in which the linkage is "weak" (Lip-

mann, 1941). Examples of the first group are phosphate esters such as glucose-6-phosphate, glyceraldehyde-3-phosphate, phosphoglyceric acid, etc. In these compounds, there is little tendency of the phosphate group to split off. The escaping tendency or group potential of the phosphate is low. When the phosphate group of these compounds is split off by hydrolysis, there is a release of relatively little energy, of the order of 3000 calories. This type of phosphate bond is known as an energy-poor phosphate bond.

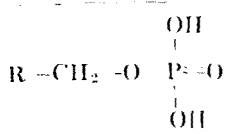
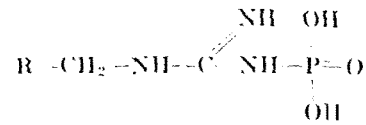
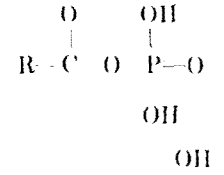
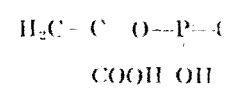
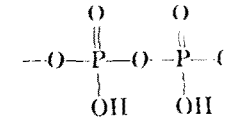
In contrast with the stable energy-poor ester bond, phosphate is found in several organic linkages which are readily split off by hydrolysis. These phosphate bonds, such as carboxyl phosphate and enol phosphate, are characterized by a high escaping tendency or high group potential, and are called high-energy phosphate bonds (~ ph). The hydrolytic rupture of a high-energy phosphate bond yields from 12,000 to 16,000 calories per mole. Thus, the potential of a high-energy bond is about four times that of a low-energy bond. The significance of the high-energy phosphate bond in metabolic reactions lies in the fact that the phosphate group can be transferred intact *together* with the high energy contained in the bond to a suitable acceptor whose free-energy level is thereby raised. As already stated, the adenylic acid system is the principal acceptor of the high-energy phosphate bonds that are generated in cellular reactions.

The phosphate bonds found in the organic compounds of living cells are summarized in Table III. The energy status of each type of bond is expressed as ΔF, signifying a change in the free energy. A negative ΔF indicates that the reaction, in this case the hydrolysis of the phosphate group, will proceed spontaneously with a release of energy.

The high-energy phosphate bond is a device for storing and transporting in cellular reactions large amounts of energy of the order from 12,000 to 16,000 calories. As pointed out by Lipmann (1951), the phosphate bond is particularly suited to perform this function in biological energy transfers because it confers "kinetic stability" in an aqueous medium "on thermodynamically labile bonds." For example, the compounds acetic anhydride, $CH_3{\cdot}C(=O){\cdot}O{\cdot}C(=O){\cdot}CH_3$, and acetyl phosphate, $CH_3{\cdot}C(=O){\cdot}O{-}P(=O)(OH){-}OH$, have approximately the same free-energy level. However, the acetic anhydride has a lifetime in water of only a few seconds, whereas acetyl phosphate can exist for several hours. Pyrophos-

TABLE III

TYPES OF PHOSPHATE BONDS IN CELLULAR METABOLITES

Type	*Structure*	*Approximate $-\Delta F$ of hydrolysis of P bond, calories per mole*	*Examples of occurrence*
Ester phosphate		2000–3000	Glucose-6-phosphate, fructose-6-phosphate, fructose-1,6,-diphosphate, glyceraldehyde-3-phosphate, phosphoglyceric acid, adenylic acid
Amidine phosphate		12,000	Arginine phosphate, creatine phosphate
Acyl phosphate		16,000	1,3-Diphosphoglyceric acid, acetyl phosphate
Enol phosphate		16,000	Phosphoenolpyruvic acid
Pyrophosphate		10,000–12,000	ATP, ADP

phate (Table III), still another compound with the same high-energy level, has an indefinite life in a water medium. This explains why the adenylic acid system with its pyrophosphate bonds is particularly well suited to act as the acceptor and donor of high-energy phosphate bonds in cellular reactions.

2. *The Role of Pyridine Nucleotides in Energy Transfer*

As already stated, the pyridine nucleotides DPN and TPN serve as electron or hydrogen carriers in oxidation-reduction reactions. Since DPN and TPN undergo reversible reductions, they can participate directly in the energy transfer in metabolic reactions by linking different enzyme systems and their respective substrates. The pattern of these reactions is as follows: oxidized DPN (or TPN), acting in con-

junction with enzyme E_1, oxidizes substrate S_1 by accepting two electrons and becomes reduced to DPN·H (or TPN·H). The reduced DPNH (or TPNH) can now reduce substrate S_2 with the aid of an appropriate enzyme E_2. In other words, the energy released by the oxidation of substrate S_1 was stored as "reducing power" in the DPNH or TPNH, which can in turn attach itself to another enzyme and bring about the reduction of another substrate. In this manner, the energy contained in one substrate can be used to perform the cellular work required for the reduction of another substrate, without the intermediary of phosphate bond energy.

An interesting example of this role of pyridine nucleotides was discovered recently in the study of photosynthesis. It was found independently in three laboratories (Vishniac and Ochoa, 1951, 1952; Tolmach, 1951a, 1951b; Arnon, 1951; Arnon and Heimbürger, 1952c) that TPN could act as an intermediary in the transformation of solar energy into chemical energy. The sequence of reactions involved first the use of light energy by illuminated chloroplasts to bring about the cleavage of water and a reduction of TPN by the hydrogen of water. The reduced TPN was then used with the "malic" enzyme to bring about the reductive carboxylation of pyruvate to malate (catalyzed by manganese). The reactions were as follows:

$$H_2O + TPN^+ \xrightarrow[\text{chloroplasts}]{\text{light}} TPNH + H^+ + \tfrac{1}{2}O_2$$

$$CH_3COCOOH + {}^{*}CO_2 + TPNH + H^+ \xrightarrow[\text{malic enzyme}]{Mn^{++}} {}^{*}COOH\cdot CH_2\cdot CHOH\cdot COOH + TPN$$

Pyruvic acid — Malic acid

Sum: $CH_3COCOOH + CO_2 + H_2O \rightarrow COOH\cdot CH_2\cdot CHOH\cdot COOH + \tfrac{1}{2}O_2$

An aspect of these linked reactions pertinent to photosynthesis is that the complete enzyme system was reconstructed *in vitro* from the constituents of green leaves (Arnon, 1951). It is not possible at this time to evaluate the role of this photochemical synthesis of malic acid in the overall scheme of photosynthesis *in vivo*. It is significant, nevertheless, that with the intermediary of TPN a linked reaction was reconstructed outside the living cell which is characterized by the salient features of photosynthesis *in vivo:* transformation of light into chemical energy and fixation of carbon dioxide with a simultaneous evolution of oxygen. Other reactions linking isolated chloroplasts to several DPN- and TPN-dependent reductions by enzyme systems derived from various sources have been demonstrated by Vishniac and Ochoa (1952).

It has recently been shown (Lehninger, 1951) that the oxidation of reduced coenzyme I (DPNH) is coupled with phosphorylation. The

transfer of electrons from reduced DPN to oxygen leads to the generation of high-energy phosphate bonds according to the reaction:

$$DPNH + 3ADP + 3PO_4 + \tfrac{1}{2}O_2 + H^+ \rightarrow DPN + 3ATP + H_2O$$

This reaction is of special interest to photosynthesis. It has already been seen that isolated chloroplasts can bring about the reduction of DPN and TPN. If the photochemically reduced pyridine nucleotides can in turn generate high-energy phosphate bonds in ATP according to the above equation, a mechanism is provided for the transformation of light energy into phosphate-bond energy. Evidence of such transformation of light energy captured by isolated chloroplasts into high-energy phosphate bond has recently been reported (Ochoa and Vishniac, 1952).

It appears, therefore, that the pyridine nucleotides occupy an important position in the energy transformations of the living cell, either through their role of electron carriers in linked enzymatic reactions, or in the transfer of electrons to oxygen with a concomitant generation of high-energy phosphate bonds. It is probable that the pyridine nucleotides will be shown to occupy a key position in the mechanism of photosynthesis *in vivo*.

VII. The Role of Phosphate in Carbohydrate Breakdown

As already pointed out in Section V.4, the release of energy resulting from the degradation of stored carbohydrates involves two phases, one anaerobic and one aerobic. In both of these phosphate plays a central role. The complete oxidation of a mole of glucose to carbon dioxide and water brings about a release of around 680,000 calories. In the first or anaerobic phase, which is represented by the series of glycolytic reactions leading from glucose to pyruvate (Fig. 4), only about 60,000 calories are released. Approximately 90 per cent of the energy contained in the glucose molecule is released in the second phase, the aerobic oxidation of pyruvate. Most of the energy released during both the glycolytic and the aerobic phase of carbohydrate degradation is converted into phosphate bond energy.

1. The Participation of Phosphate in Glycolysis

The participation of phosphate in the glycolytic degradation of carbohydrates can be divided into the incorporation of inorganic phosphate into organic linkages, the generation of high-energy phosphate bonds, and the transfer of high-energy phosphate bonds to the adenylic acid system. The utilization of the high-energy phosphate bonds and the

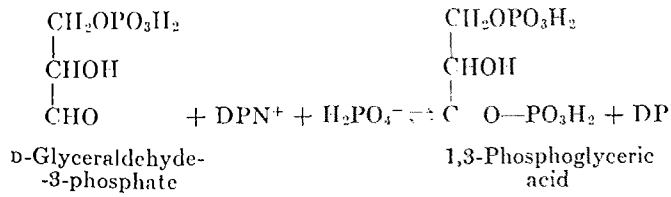
regeneration of inorganic phosphate will be discussed in Sections VIII and IX.

As shown in Fig. 4, inorganic phosphate is incorporated in reactions 1 and 8. In reaction 1 catalyzed by phosphorylase, the straight-chain component of starch, *amylose*, is converted into glucose-1-phosphate (Hassid, 1951) in accordance with the reversible reaction:

$$\text{Amylose} + PO_4 \rightleftharpoons \text{Glucose-1-phosphate}$$

In the forward reaction, inorganic phosphate disrupts the 1-4 glycosidic bonds (—C—O—C—) which link glucose molecules to form the polysaccharide. The disruption of the glycosidic bonds by phosphorylase with inorganic phosphate is analogous to the hydrolytic cleavage of starch by amylase, in which the glycosidic bonds are disrupted by water molecules. However, the substitution of phosphorylysis for hydrolysis has the important consequence that the energy originally expended in the synthesis of the glycosidic bond during the formation of starch is not dissipated but is preserved in glucose-1-phosphate, which in turn can be further degraded, as shown in Fig. 4. Free glucose requires, before it can be further metabolized, an initial phosphorylation by hexokinase (reaction 3, Fig. 4) in which one high-energy phosphate bond from ATP is consumed.

The series of reactions from 1 to 7 in Fig. 4 represent no net release of the energy stored in the carbohydrate molecule. In reaction 8 however, the triose, D-glyceraldehyde-3-phosphate, is oxidized to phosphoglyceric acid with a simultaneous uptake of inorganic phosphate. This gives rise to the formation of an energy-rich acyl phosphate group. The reaction is catalyzed by glyceraldehyde phosphate dehydrogenase according to the reaction (Meyerhof, 1944):



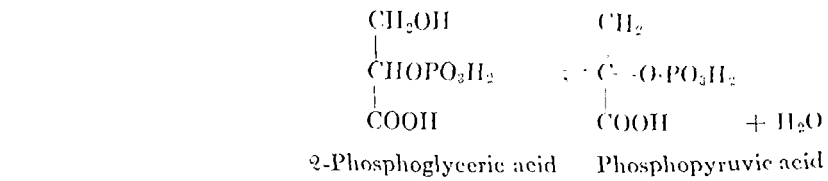
The energy-rich acyl phosphate group from the 1,3-diphosphoglyceric acid is transferred by phosphoglyceric acid kinase to ADP, giving rise to ATP in accordance with reaction 9 (Fig. 4):

$$\text{1,3-Phosphoglyceric acid} + ADP \rightleftharpoons \text{3-Phosphoglyceric acid} + ATP$$

Glyceraldehyde phosphate dehydrogenase is known as the oxidizing enzyme of glycolysis. The activity of this enzyme accounts for the up-

take of inorganic phosphate in fermentation. The enzyme h isolated in crystalline form from yeast (Warburg and Christian and from rabbit muscle (Cori, Slein, and Cori, 1948) and was be DPN-specific. There was some doubt about the existence enzyme in green leaves (Stumpf, 1952a; Albaum, 1952). Re dence, however, has demonstrated the existence of glyceraldehy phate dehydrogenase in green plants (Gibbs, 1952; Arnon 1952b). The leaf enzyme was found, unlike its counterpart in y muscle, to be able to oxidize glyceraldehyde phosphate with eitl or TPN. This observation is of special interest because of the fi Whatley (1951) that TPN rather than DPN is the principal nucleotide in green leaves.

The oxidation of phosphoglyceraldehyde illustrates a mc for the storage, in the form of high-energy phosphate bond energy released in cellular oxidation. With one exception, the of high-energy phosphate bonds is always associated with o The sole exception known today is reaction 11 (Fig. 4), cata enolase according to the reaction:



The dehydration of the 2-phosphoglyceric acid gives ri formation of an energy-rich enol phosphate bond in phosph acid. The energy-rich phosphate group of phosphopyruvic acid ferred to ADP by pyruvic acid kinase, according to reaction 12 In this manner another molecule of ATP is generated.

The transformation of one molecule of triose phosphate to thus results in the formation of two (~ ph), or four (~ ph molecule of glucose. The ΔF of the oxidation giving rise to phosphate group in reaction 8 is —16,500 calories (Meyerh and the ΔF of the enol phosphate group in reaction 11 is calories (Kaplan, 1951). The total energy released during per mole of glucose is therefore equal to 2(16,500 + 16,000) calories per mole. On the basis of a (~ ph) value in ATP calories per mole the formation of (~ ph) in the conversion to pyruvic acid represents a conversion of $\frac{(4 \times 12{,}000)}{65{,}000} \times$ per cent of released energy into phosphate bond energy.

Of the four (~ ph) formed during glycolysis, two (~ ph

sumed in the phosphorylation of the glucose molecule by reactions 3 and 5 (Fig. 4). The net yield consists therefore of two (~ ph) per molecule of glucose. This can be summarized in the following manner:

$$\begin{array}{l} \text{Glucose} + 2\,\text{ATP} \rightarrow \text{Fructose diphosphate} + 2\,\text{ADP} \\ \text{Fructose diphosphate} + 2H_2PO_4^- + 4\,\text{ADP} \rightarrow 2\,\text{pyruvate} + 4\,\text{ATP} \\ \hline \text{Sum: Glucose} + 2H_2PO_4^- + 2\,\text{ADP} \rightarrow 2\,\text{pyruvate} + 2\,\text{ATP} \end{array}$$

It appears from Fig. 4 that, if starch (amylose) rather than glucose is used as a substrate for glycolysis, the net yield of (~ ph) per molecule of glucose is three rather than two, since the hexokinase reaction 3 (Fig. 4), which consumes one molecule of ATP, is replaced by the phosphorylase reaction 1, in which inorganic phosphate is absorbed. This conclusion, although it accords with the facts, has only superficial plausibility. A (~ ph) has been consumed in the synthesis of the glycosidic linkage in the formation of starch (glucose to starch, via reactions 3, 2, and 1). There is thus no overall increase in the energy yield to the cell by replacing glucose with starch as the substrate for glycolysis.

2. *Aerobic Phosphorylation of Pyruvate*

The complete aerobic oxidation of pyruvate to carbon dioxide and water proceeds by way of the Krebs tricarboxylic acid cycle (Krebs, 1943). The oxidation of one molecule of pyruvate involves the transfer of five pairs of electrons to oxygen. Since one mole of glucose gives rise to two of pyruvate, the overall reaction can be represented (Kaplan, 1951) as:

$$2\,\text{pyruvate} + 5O_2 \rightarrow 6CO_2 + 10H_2O + 590{,}000\ \text{calories}$$

There is now ample evidence, reviewed by Hunter (1951), that the energy released during the oxidation of pyruvate is converted into energy-rich phosphate bonds. The problem has been studied by measuring the relative amounts of oxygen consumed (expressed as O, not O_2) and of inorganic phosphate (expressed as P) incorporated into organic compounds (P:O ratio). The P:O ratio varies with different substrates in the Krebs cycle. A P:O ratio greater than 1 signifies that not only the oxidation of the substrate but also some of the further steps in electron transfer may be coupled to phosphorylations. There is now general agreement that the complete oxidation of pyruvate is accompanied by fifteen phosphorylations. This gives an average of three phosphorylations for each of the five oxidative steps in the metabolism of pyruvate by the Krebs cycle. The actual breakdown of the number of phosphorylations among the five steps is as follows (Hunter, 1951):

(1) Pyruvate + Oxalacetate + $\frac{1}{2}O_2$	→ Citrate + CO_2	3
(2) Isocitrate + TPN	→ Oxalosuccinate + TPNH	0
TPNH + $\frac{1}{2}O_2$	→ TPN + H_2O	3
(3) α-Ketoglutarate + $\frac{1}{2}O_2$	→ Succinate + CO_2	4
(4) Succinate + $\frac{1}{2}O_2$	→ Fumarate + H_2O	2
(5) Malate + DPN	→ Oxalacetate + DPNH	0
DPNH + $\frac{1}{2}O_2$	→ DPN + H_2O	3
	Total	15

The association of phosphorylation with aerobic oxidation was found to be linked with the transfer of electrons from DPNH or TPNH to oxygen. It has already been stated under Section VI.2 that Lehninger (1951) obtained direct evidence for the coupling of phosphorylation to the oxidation of DPNH. The values for the P:O ratio suggest that three high-energy phosphate bonds are formed during the reaction.

The preceding discussion has indicated that most of the energy released during the oxidation of glucose is stored in the form of high-energy phosphate groups in ATP. The total number of these groups formed by the oxidation of 1 mole of glucose can be computed as follows:

From glycolysis (cf. Section VII.1)	2
From oxidation of 2 DPNH (cf. reaction 8, Fig. 4)	6
From oxidation of 2 pyruvate	30
	38

On the basis of 12,000 calories for the pyrophosphate ATP bond (Table III), the conversion of the energy released during the complete oxidation of glucose to CO_2 and water is of a high order of efficiency:

$$\frac{38 \times 12{,}000}{680{,}000} \times 100 = 67\%$$

In animal tissues, the enzymes responsible for oxidative phosphorylation were found to be located in insoluble particles of the cytoplasm, such as mitochondria (see reviews in McElroy and Glass, 1951). Until recently, there was no direct evidence for the existence of parallel enzyme systems in higher plants. This gap in our knowledge has now been filled by the report of Millerd *et al.* (1951) that mitochondrial particles from mung beans contain an enzyme system capable of the complete oxidation, via the Krebs cycle, of pyruvate to carbon dioxide and water.

VIII. The Role of Phosphate in Carbohydrate Synthesis

1. Synthesis of Polysaccharides

The hydrolytic enzymes invertase and amylase, which act on sucrose and starch, can bring about the cleavage but not the synthesis of gly-

cosidic linkages (—C—O—C—). This is the result of the high molarity of water, in the aqueous reaction medium. According to Colowick (cited by Kaplan, 1951) the energy requirement for overcoming the high concentration of water is $\Delta F = 2500$ calories per mole. The energy for accomplishing cellular synthesis is provided in the main by ATP in the presence of specific enzymes which catalyze the transfer of the phosphate groups. The synthesis of starch from glucose is accomplished in three steps: the phosphorylation of glucose by ATP in the presence of hexokinase to form glucose-6-phosphate (reaction 3, Fig. 4), the conversion of glucose-6-phosphate to glucose-1-phosphate by phosphoglucomutase (reaction 2, Fig. 4), and the condensation by phosphorylase of glucose-1-phosphate units to form glycosidic linkages with the elimination of phosphate (reaction 1, Fig. 4). In the synthesis of glycosidic linkages approximately 9000 calories are lost, since the energy of these bonds is only 3000 calories and that of the (~ ph) of ATP is 12,000 calories. Each glucose unit of starch possesses 3000 calories of free energy in addition to the free energy of a free glucose molecule. As already pointed out, the phosphorylation breakdown of starch, which involves the uptake of inorganic phosphate, preserves this extra energy in the phosphate bond of glucose-1-phosphate. The glycosidic linkages of starch thus represent a reservoir of stored energy, which can be released by phosphate.

The formation of starch illustrates the pattern involved in cellular syntheses with the aid of ATP. The mechanism usually involves at least two steps, one of which is the transfer of a (~ ph) from ATP to one of the reactants, and the other the condensation of a phosphorylated product with another molecule. The condensation results in the liberation of inorganic phosphate. The net result as far as the phosphate is concerned is an hydrolysis of a (~ ph) of ATP with a transfer of some of the energy of the bond to the synthesized compound which has been raised to a higher energy level than the unphosphorylated reactants. The inorganic phosphate has undergone a cycle, being first incorporated in an organic linkage to form a new (~ ph) in ATP, and then released when the energy of (~ ph) was consumed in the performance of cellular work.

2. Phosphate in Photosynthesis

It has been one of the common assumptions in plant physiology that photosynthesis in its overall aspect must be a reversal of respiration. With the elucidation of the biochemical reactions in fermentation and respiration, this point of view was expressed in more concrete terms by Thimann (1938). He suggested that the initial fixation of carbon dioxide

was a carboxylation of some product of glycolysis, an aldehyde or an organic acid, followed by a photochemical reduction of the carboxyl group. Thimann further suggested that basically the same mechanism may be operative in carbon dioxide fixation by all autotrophic organisms, photosynthetic as well as chemosynthetic.

The hypothesis that the formation of sugar in photosynthesis involves a reversal of the degradative reactions of respiration received strong experimental support from the work of Benson and Calvin (1950), who, with the aid of radioactive carbon, identified, among the newly synthesized products of short-time photosynthesis, organic phosphorus compounds which were known intermediates of glycolysis. In very short periods of photosynthesis, of the order of several seconds, most of the newly fixed $C^{14}O_2$ was found in the carboxyl of phosphoglyceric acid. With increasing exposure to light the proportion of total radioactivity fixed in the phosphoglycerate decreased, and newly fixed carbon dioxide was detected in a relatively large array of compounds, including triosephosphate, hexose diphosphate, and sucrose. The identification of the main product of early photosynthesis as phosphoglycerate was confirmed by Gaffron, Fager, and Rosenberg (1951).

The participation of phosphorus in the intermediate reactions of photosynthesis was demonstrated directly by the simultaneous use of radioactive phosphorus and carbon isotopes in the same experiment. The radioactive phosphorus compounds were identified by means of radioautographic techniques. Buchanan *et al.* (1952) suspended the alga *Scenedesmus* in a solution containing radioactive phosphate for twenty hours prior to exposure to light. Upon exposure to light, bicarbonate labeled with C^{14} was introduced and photosynthesis was allowed to proceed for five minutes. The algae were then killed and extracted with alcohol, and an aliquot of the extract was assayed by paper chromatography. Two sheets of X-ray film were placed on the developed paper chromatograms, the one next to the paper being used to screen out the low-energy beta particles emitted by the carbon atoms. The top film was thus affected only by the beta particles from the radioactive phosphorus. Since the half-life of P^{32} is relatively short (fourteen days), it was feasible to allow, by a suitable waiting period, for a decay of the radioactive phosphorus on the paper chromatogram. A fresh radioautograph was then made showing only the radioactive carbon. By superimposing the carbon radioautograph on the phosphorus radioautograph, it was possible to identify the compounds which had become labeled with both tracers (Figs. 5 and 6).

The list of phosphorus compounds formed during early photosynthesis has been extended by Buchanan *et al.* (1952). The list now in-

cludes Fig. 7 sedoheptulose phosphate, pentose phosphate, phosphoglycolic acid, and phosphopyruvic acid, and evidence was obtained for the formation of sucrose phosphate, and the nucleotides uridine diphosphate glucose (UDPG), uridine diphosphate galactose, ATP, and a compound giving mannose on hydrolysis.

In addition to the identification of phosphorylated compounds as intermediates in photosynthesis, there is converging evidence from sev-

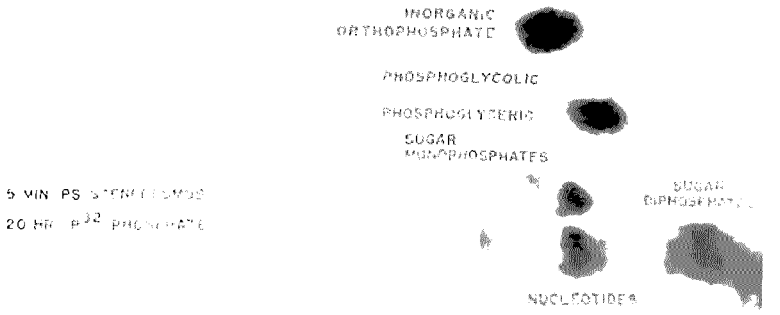


FIG. 5. Radioautograph of extract of *Scenedesmus* grown for twenty hours in radioactive phosphate and then allowed to carry on photosynthesis in $C^{14}O_2$ for five minutes. A sheet of exposed film was used to filter out the C^{14} radiation (Buchanan *et al.*, 1952).

eral investigations about the participation of phosphate in photosynthesis. Evidence has already been cited in Section VI.2 for the conversion of light energy into high-energy phosphate bonds through the intermediary of isolated chloroplasts. Kandler (1950) found enhanced utilization of inorganic phosphate following illumination of *Chlorella*. There is also evidence that a large proportion of the newly absorbed phosphate in short-time photosynthesis is incorporated in phosphoglyceric acid and that ATP is rapidly utilized in photosynthetic reactions (Goodman *et al.* 1952; Strehler, 1952).

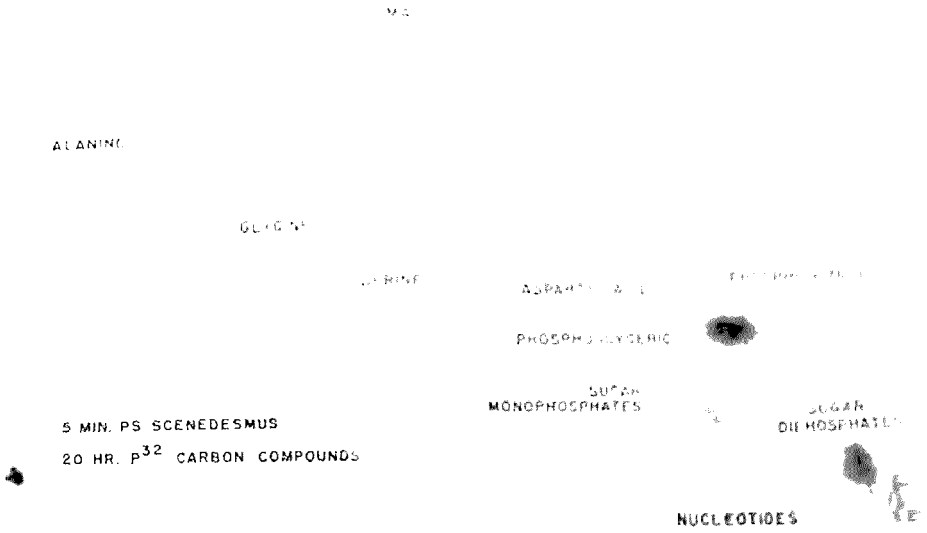


FIG. 6. Radioautograph of the same extract as in Fig. 5. The exposure was made after the phosphorus radiation had decayed (Buchanan *et al.*, 1952).

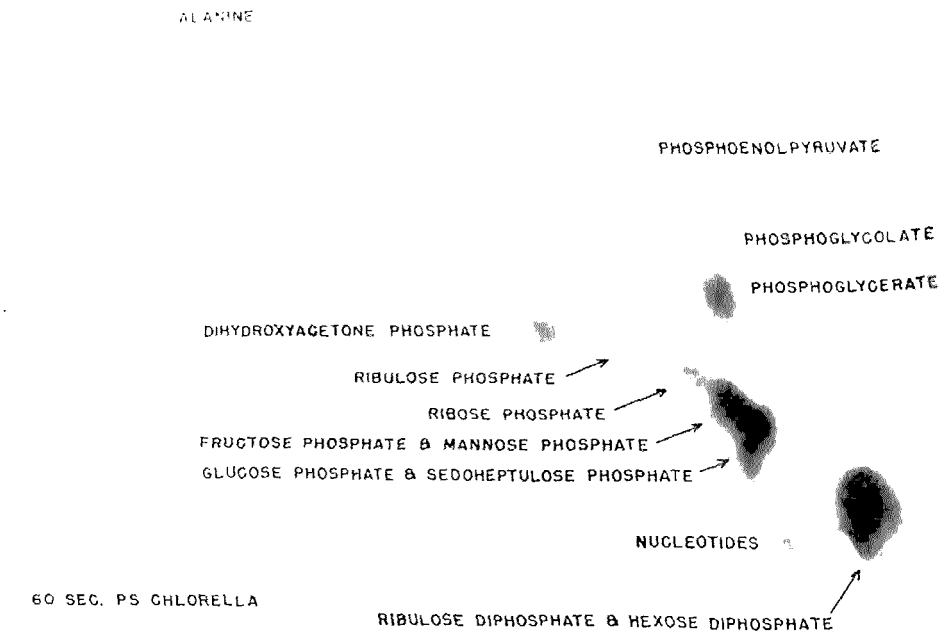


FIG. 7. Phosphorus compounds formed during early photosynthesis (Buchanan *et al.*, 1952).

The intimate association of phosphate with photosynthesis necessitates a realignment of traditional concepts of plant nutrition. It has been often assumed in the past that carbon dioxide assimilation in photosynthesis proceeds by an autonomous path without a direct participation of the inorganic elements absorbed by the roots from the soil. The term mineral nutrition has been used to describe the events associated with the absorption and utilization of inorganic elements derived from the root environment. It appears however, that mineral nutrition and photosynthesis can no longer be treated separately. In the early events of photosynthesis, phosphate assimilation cannot be separated from carbon assimilation. There is little doubt that, as our knowledge of photosynthesis advances, other intimate relations between the inorganic elements derived from the root environment and the assimilation of carbon, will come to light.

IX. Utilization of Phosphate Bond Energy

The preceding discussion has already indicated the versatility of the high-energy phosphate bond as the intermediary of energy transformations in the living cell. Phosphate bond energy has been shown to be used in mechanical work such as muscle contraction, in the emission of light by luminous organisms, in the production of bioelectricity, and in the multitude of chemical reactions in the cell in which energy is consumed or work is accomplished (McElroy and Glass, 1951). The synthesis of cellular constituents is accomplished by endergonic reactions in which there is an increase in free energy (ΔF)—that is, the reactants are converted into products of higher energy levels. These reactions are driven by the phosphate bond energy of ATP. The synthesis of starch from glucose has already been discussed in Section VIII.1 as a model of these reactions. As another example, the conversion of fructose to glucose can also be accomplished at the expense of the phosphate bond energy of ATP by means of the three reactions:

$$\text{Fructose} + \text{ATP} \xrightarrow{\text{hexokinase}} \text{Fructose-6-phosphate}$$

$$\text{Fructose-6-phosphate} \xrightarrow{\text{phosphohexoisomerase}} \text{Glucose-6-phosphate}$$

$$\text{Glucose-6-phosphate} \xrightarrow{\text{phosphatase}} \text{Glucose}$$

In reaction 3 of Fig. 4, hexokinase has been cited as the enzyme responsible for the phosphorylation of glucose. The same enzyme from certain sources, as for example yeast, is also able to phosphorylate fructose. Phosphatase is one of a group of widely distributed hydrolyzing enzymes which split off inorganic phosphate without any associated synthetic reactions.

Many other examples of the use of phosphate bond energy to perform chemical work have come to light from work on animal tissues. There is increasing evidence that parallel mechanisms operate in plants. The synthesis of amides and fatty acids by plant tissues is a case in point (Stumpf, 1952b).

Work against osmotic forces can also be accomplished at the expense of phosphate bond energy. Let us assume that the cytoplasmic membrane is permeable to substance S in its free form but not to the phosphorylated compound S-p. S would then enter the cell freely by diffusion. If inside the cell S were phosphorylated to S-p by ATP with the aid of the proper phosphokinase, the concentration of *free* S would be maintained low and the thermodynamic gradient would favor the continued absorption of S from the outside. There is evidence (Sinclair, 1939) that a mechanism of this sort operates for thiamine (vitamin B_1). Thiamine occurs in the free form in blood plasma, but after it is absorbed by the blood cells it is phosphorylated to thiamine pyrophosphate (cocarboxylase) and is trapped in this manner inside the cells. The concentration of thiamine pyrophosphate inside the cell is several times higher than the concentration of free thiamine in the blood plasma. In this instance, therefore, the energy of the phosphate bond in ATP is used to bring about an accumulation of thiamine against a concentration gradient.

It seems probable that similar mechanisms will be shown to operate in the absorption and translocation of inorganic and organic nutrients by plants. The transport of organic substances could be visualized by analogy with the mechanism just described. As for the accumulation of inorganic ions, phosphorylated intermediates could act as carriers (Overstreet and Jacobson, 1952) or trapping agents of anions or cations. Oxidative metabolism, known to be indispensable for ion accumulation, would serve as the source of ATP (see Section VII.2), at the expense of which the phosphorylated intermediates would be formed.

Although such postulations are at this time supported only by theoretical considerations, there are already indications that phosphate bond energy may be involved in the process of ion accumulation. Loomis and Lipmann (1948) have shown that 2,4-dinitrophenol dissociates ATP formation from cellular oxidation. In low concentration dinitrophenol stimulates respiration while abolishing phosphorylation. This inhibitor can thus be used to determine whether certain reactions require phosphate bond energy. Robertson *et al.* (1951) have recently found that dinitrophenol, while increasing the respiration, inhibited the accumulation of ions by carrot cells.

REFERENCES

ALBAUM, H. G. 1952. The metabolism of phosphorylated compounds in plants. *Ann. Rev. Plant Physiol.* **3**: 35–38.

ALBAUM, H. G., and UMBREIT, W. W. 1943. Phosphorus transformations during the development of the oat embryo. *Am. J. Botany* **30**: 553–558.

ARNON, D. I. 1939. Effect of ammonium and nitrate nitrogen on the mineral composition and sap characteristics of barley. *Soil Sci.* **48**: 295–307.

ARNON, D. I. 1951. Extracellular photosynthetic reactions. *Nature* **167**: 1008–1010.

ARNON, D. I. 1952a. Glyceraldehyde phosphate dehydrogenase of green plants. *Science* **116**: 635–637.

ARNON, D. I. 1952b. The glycolytic cycle in the breakdown and synthesis of carbohydrates in green plants. *In* Phosphorus Metabolism, Vol. II, pp. 67–79. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

ARNON, D. I., FRATZKE, W. E., and JOHNSON, C. M. 1942. Hydrogen ion concentration in relation to absorption of inorganic nutrients by higher plants. *Plant Physiol.* **17**: 515–524.

ARNON, D. I., and HEIMBERGER, GUNILLA. 1952. Extracellular photosynthetic reactions II. Identification of radioactive malate. *Plant Physiol.* **27**: 828–833.

ARNON, D. I., and HOAGLAND, D. R. 1943. Composition of the tomato plant as influenced by nutrient supply, in relation to fruiting. *Botan. Gaz.* **104**: 576–590.

ARNON, D. I., and JOHNSON, C. M. 1942. Influence of hydrogen ion concentration on the growth of higher plants under controlled conditions. *Plant Physiol.* **17**: 525–539.

ARNON, D. I., STOUT, P. R., and SIPOS, F. 1940. Radioactive phosphorus as an indicator of phosphorus absorption of tomato fruits at various stages of development. *Am. J. Botany*, **27**: 791–798.

BANGA, I., and SZENT-GYÖRGYI, A. 1932. Über Co-Fermente, Wasserstoff-donatoren und Arsenvergiftung der Zellatmung. *Biochem. Z.* **246**: 203–214.

BANGA, I., SZENT-GYÖRGYI, A., and VARGHA, L. 1932. Über das Co-Ferment der Milchsäureoxydation. *Z. physiol. Chem.* **210**: 228–235.

BENSON, A. A., and CALVIN, M. 1950. Carbon dioxide fixation by green plants. *Ann. Rev. Plant Physiol.* **1**: 25–42.

BIDDULPH, O. 1951. The translocation of minerals in plants. *In* Mineral Nutrition of Plants, pp. 261–275. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

BINGHAM, F. T. 1951. Integration of soluble phosphorus, pot tests and field experiments. Ph.D. Thesis, University of California, Berkeley, California.

BUCHANAN, J. G., BASSHAM, J. A., BENSON, A. A., BRADLEY, D. F., CALVIN, M., DAUS, L. L., GOODMAN, M., HAYES, P. M., LYNCH, V. H., NORRIS, L. T., and WILSON, A. T. 1952. The path of carbon in photosynthesis. XVII. Phosphorus compounds as intermediates in photosynthesis. *In* Phosphorus Metabolism, Vol. II, pp. 440–459. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

COHEN, S. S. 1951. The role of the oxidative pathway of glucose-6-phosphate degradation in growing and virus-infected *E. coli*. *In* Phosphorus Metabolism, Vol. II, pp. 148–158. W. D. McElroy and B. Glass, Editors, Johns Hopkins Press, Baltimore.

COLOWICK, S. P. 1951. Transphosphorylating enzymes of fermentation. *In* The Enzymes, Vol. II, Pt. 1, pp. 114–150. J. B. Sumner and K. Myrbäck, Editors. Academic Press, New York.

CORI, G. T., SLEIN, M. W., and CORI, C. F. 1948. Crystalline triphosphopyridine nucleotide dehydrogenase from rabbit muscle. *J. Biol. Chem.* **173**: 605–618.

DEAN, L. A. 1949. Fixation of soil phosphorus. *Advances in Agron.* **1**: 391–411.

GAFFRON, H., FAGER, E. W., and ROSENBERG, J. L. 1951. Intermediates in photosynthesis. Formation and transformation of phosphoglyceric acid. *Symposia Soc. Exptl. Biol.* **5**: 262–283.

GERICKE, W. F. 1924. The beneficial effect to wheat growth due to depletion of available phosphorus in the culture media. *Science* **60**: 297–298.

GIBBS, M. 1952. Triosephosphate dehydrogenase and glucose-6-phosphate dehydrogenase in the pea plant. *Nature* **170**: 164–165.

HASSID, W. Z. 1951. Metabolism of polysaccharides and disaccharides. *In* Phosphorus Metabolism, Vol. I. pp. 11–42. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

HOAGLAND, D. R. 1944. Lectures on the Inorganic Nutrition of Plants. Chronica Botanica, Waltham, Mass.

HOAGLAND, D. R., and MARTIN, J. C. 1923. A comparison of sand and solution cultures with soils as media for plant growth. *Soil Sci.* **16**: 366–388.

HORECKER, B. L. 1951. The metabolism of pentose and triose phosphates. *In* Phosphorus Metabolism, Vol. I, pp. 117–144. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

HUNTER, F. E., JR. 1951. Oxidative phosphorylation during electron transport. *In* Phosphorus Metabolism, Vol. I, pp. 297–330. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

KALCKAR, H. M. 1941. The nature of energetic coupling in biological syntheses. *Chem. Revs.* **28**: 71–178.

KANDLER, O. 1950. Über die Beziehungen zwischen Phosphathaushalt und Photosynthese. *Z. Naturforsch.* **5b**: 432–437.

KAPLAN, N. O. 1951. Thermodynamics and mechanism of the phosphate bond. *In* The Enzymes, Vol. I, Pt. 1, pp. 55–113. J. B. Sumner and K. Myrbäck, Editors. Academic Press, New York.

KORNBERG, A. 1951. The metabolism of phosphorus-containing coenzymes. *In* Phosphorus Metabolism, Vol. I, p. 392. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

KREBS, H. A. 1943. The intermediary stages in the biological oxidation of carbohydrate. *Advances Enzymol.* **3**: 191–252.

LEHNINGER, A. L. 1951. Phosphorylation coupled to oxidation of dihydrodiphosphopyridine nucleotide. *J. Biol. Chem.* **190**: 345–359.

LELOIR, L. F. 1951. The metabolism of hexose phosphates. *In* Phosphorus Metabolism, Vol. I, pp. 67–93. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press. Baltimore.

LIPMANN, F. 1941. Metabolic generation and utilization of phosphate bond energy. *Advances in Enzymol.* **1**: 99–162.

LIPMANN, F. 1951. The chemistry and thermodynamics of phosphate bonds: Introductory remarks. *In* Phosphorus Metabolism, Vol. I, pp. 521–522. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

LOOMIS, W. F., and LIPMANN, F. 1948. Reversible inhibition of the coupling between phosphorylation and oxidation. *J. Biol. Chem.* **173**: 807–808.

MARTIN, W. E., and BUCHANAN, J. R. 1950. Phosphate test for grain land. *Calif. Agr.*, **4**: 7, 12.

MEYERHOF, O. 1944. Energy relationships in glycolysis and phosphorylation. *Ann. N.Y. Acad. Sci.* **45**: 377–393.

MILLERD, A. BONNER, J., AXELROD, B., and BANDURSKI, R. 1951. Oxidative and phosphorylative activity of plant mitochondria. *Proc. Natl. Acad. Sci. U. S.* **37**: 855–862.

MCAULIFFE, C. D., HALL, N. S., DEAN, L. A., and HENDRICKS, S. B. 1947. Exchange reactions between phosphates and soils: hydroxylic surfaces of soil minerals. *Soil Sci. Soc. Amer. Proc.* **12**: 119–123.

MCCANCE, R. A., and WIDDOWSON, ELSIE M. 1935. Phytin in human nutrition. *Bioch. J.* **29**: 2694–2699.

MCELROY, W. D., and GLASS, B. 1951. Phosphorus Metabolism. Vol. I. Johns Hopkins Press, Baltimore.

MCELROY, W. D., and GLASS, B. 1952. Phosphorus Metabolism. Vol. II. Johns Hopkins Press, Baltimore.

OCHOA, S., and VISHNIAC, W. 1952. Carboxylation reactions and photosynthesis. *Science* **115**: 297–301.

OVERSTREET, R., and DEAN, L. A. 1951. The availability of soil anions. *In* Mineral Nutrition of Plants. p. 79. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

OVERSTREET, R., and JACOBSON, L. 1952. Mechanisms of ion absorption by roots. *Ann. Rev. Plant Physiol.* **3**: 189–206.

PARKER, F. W. 1927. Soil phosphorus studies: III. Plant growth and the absorption of phosphorus from culture solutions of different phosphate concentrations. *Soil Sci.* **24**: 129–146.

PARKER, F. W., and PIERRE, W. H. 1928. The relation between the concentration of mineral elements in a culture medium and the absorption and utilization of those elements by plants. *Soil Sci.* **25**: 337–343.

PIERRE, W. H., and POHLMAN, G. G. 1933. Preliminary studies of the exuded plant sap and the relation between the composition of the sap and the soil solution. *J. Am. Soc. Agron.* **25**: 144–159.

ROBERTSON, R. N., WILKINSON, M. J., and WEEKS, D. C. 1951. Studies in the metabolism of plant cells. Part IX. *Australian J. Sci. Research* **B4**: 248–264.

SCHLENK, F. 1951. Codehydrogenases I and II and apoenzymes. *In* The Enzymes. Vol. II, pp. 250–315. J. B. Sumner and K. Myrbäck, Editors. Academic Press, New York.

SINCLAIR, H. M. 1939. The estimation of Vitamin B_1 in cerebro-spinal fluid. *Biochem. J.* **33**: 1816–1821.

STOUT, P. R., and HOAGLAND, D. R. 1940. Upward and lateral movement of salt in certain plants as indicated by radioactive isotopes of potassium, sodium and phosphorus absorbed by roots. *Am. J. Botany* **26**: 320–334.

STOUT, P. R., MEAGHER, W. R., PEARSON, G. A., and JOHNSON, C. M. 1951. Molybdenum nutrition of crop plants. I. The influence of phosphate and sulfate on the absorption of molybdenum from soils and solution cultures. *Plant and Soil* **3**: 51–87.

STREHLER, B. L. 1952. Photosynthesis-energetics and phosphate metabolism. *In* Phosphorus Metabolism, Vol. II, pp. 491–502. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

STUMPF, P. K. 1952a. Glycolytic enzymes in higher plants. *Ann. Rev. Plant Physiol.* **3**: 17–34.

STUMPF, P. K. 1952b. Phosphate metabolism of plants. *In* Phosphorus Metabolism,

Vol. II, 29–67. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

TEAKLE, L. J. H. 1928. Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* **25**: 143–162.

THEORELL, H. 1937. Die freie Eiweisskomponente des gelben Ferments und ihre Kupplung mit Lactoflavinphosphorsaüre. *Biochem. Z.* **290**: 293–303.

THIMANN, K. V. 1938. The absorption of carbon dioxide in photosynthesis. *Science* **88**: 506–507.

TIDMORE, J. W. 1930. Phosphate studies in solution cultures. *Soil Sci.* **30**: 13–31.

TOLMACH, L. J. 1951a. Effects of triphosphopyridine nucleotide upon oxygen evolution and carbon dioxide fixation by illuminated chloroplasts. *Nature* **167**: 946–948.

TOLMACH, L. J. 1951b. The influence of triphosphopyridine nucleotide and other physiological substances upon oxygen evolution from illuminated chloroplasts. *Arch. Biochem.* **33**: 120–142.

VISHNIAC, W., and OCHOA, S. 1952. Fixation of carbon dioxide coupled to photochemical reduction of pyridine nucelotides by chloroplast preparations. *J. Biol. Chem.* **195**: 75–93.

VISHNIAC, W., and OCHOA, S. 1951. Photochemical reduction of pyridine nucleotides by spinach grana and coupled carbon dioxide fixation. *Nature* **167**: 768–769.

WARBURG, O., and CHRISTIAN, W. 1932. Über ein neues Oxydationsferment und sein Absorptionsspektrum. *Biochem. Z.* **254**: 438–458.

WARBURG, O., and CHRISTIAN, W. 1939. Isolierung and Kristallisation des Proteins des oxydierenden Gärungferments. *Biochem. Z.* **303**: 40–68.

WHATLEY, F. R. 1951. Coenzymes in plants. *New Phytologist* **50**: 244–257.

CHAPTER II

Soil-Plant Relationships in the Phosphorus Nutrition of Plants

L. A. DEAN and MAURICE FRIED

I. Introduction

Our present agriculture is based upon the growing of crops in the soil. The soil acts as an anchorage for plants and as a medium for entrapment and storage of water. Mineral nutrient requirements are supplied through the soil, and large but dilute mineral resources are utilized. The microbiological population resident in the soil supplies nutrients through the decomposition of plant and animal wastes and the fixation of atmospheric nitrogen; thus, the plant-soil system would appear to make efficient use of our natural resources. Current high productivity standards of economic crop production, as brought about by the use of fertilizers, improved crops, and enlightened soil management, have made new demands on the efficiency of the soil-plant system.

The problems dealing with the provision of adequate phosphorus nutrition through the medium of the soil are among the most interesting. The present discussion is limited to the specific phases pertaining to soil-plant relationships. The absorption of phosphorus by plants is the result of a multiplicity of processes taking place in the plant, in the soil, and at the root surfaces or interfacial boundaries. The subject of soil-plant relationships deals with the interdependence of these processes.

II. Phosphorus Uptake from Soils

A first approach to the subject of the phosphorus nutrition of plants leads to a consideration of the amounts and rates of absorption. Such studies will indicate something of the requirements imposed upon the soil as a source of supply.

Crops have been sampled and analyzed to determine the total amount of phosphorus absorbed. This quantity is surprisingly constant. The total amount of phosphorus absorbed by crops is seldom less than 10 or greater than 50 pounds P_2O_5 per acre per crop.

The total amount of phosphorus absorbed can be represented as the product of crop yield times composition. These factors of growth and

plant composition are not wholly independent of each other. Williams (1948) visualized the major determinants of phosphorus uptake by plants as being (1) the demand set up by the growth and normal functioning of various plant parts and (2) the external concentration or supply of the nutrient. A variety of factors have been shown to affect the mineral composition of plants. These include species and varieties of plants, soil composition, fertilizer application, and climate. Beeson (1941) has prepared a review dealing with this subject.

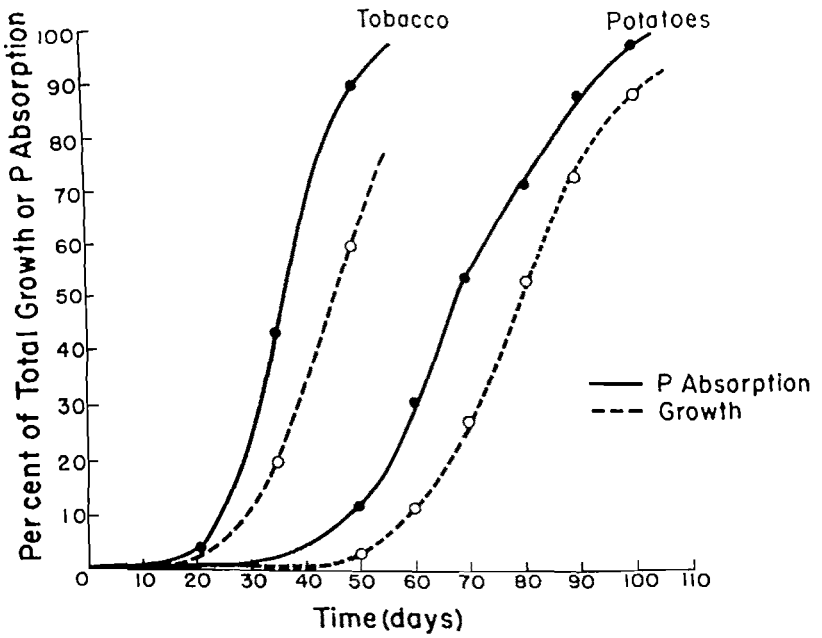


FIG. 1. Rate of phosphorus absorption and rate of growth for tobacco and potatoes (data by Grizzard *et al.*, 1942, and Hawkins, 1946).

The rate of nutrient absorption by plants has been measured by sampling and analyzing at various stages of growth. Such studies have been undertaken for a number of crops. Hawkins (1946) used potatoes; Grizzard *et al.* (1942), tobacco; Hester (1938), tomatoes; Olson and Bledsoe (1942), cotton; and Remy (1938), small grains. If the amounts of phosphorus absorbed are plotted against time a family of characteristic sigmoid curves are obtained. The rate of absorption starts out low, increases rapidly to a maximum, and then declines. Hawkins (1946) reported for potatoes a maximum rate of absorption of 0.6 pound P_2O_5 per acre per day. Williams (1948) noted that with increasing phosphorus concentration the time required to reach the maximum rate of absorption was lessened.

The rate of phosphorus absorption reaches its maximum earlier in the growth cycle than does the growth rate. This is shown in Fig. 1. For example, at a time when 50 per cent of the total phosphorus has been absorbed, only about 20 per cent of the total growth has occurred.

A common observation is that, under conditions of moderate phosphate deficiency, growth increases resulting from phosphate fertilization are observed only in the very early growth stages. At this critical stage the total amount of phosphorus being absorbed per unit of time is small. However, the amount absorbed per unit of crop growth is higher than at the later stages of growth.

Recent studies involving the use of P^{32} have supplied additional information regarding the influence of soil and fertilizer phosphorus on phosphorus absorption by crops (Spinks and Barber, 1947; Nelson *et al.*, 1947; Jacob *et al.*, 1949; Woltz *et al.*, 1949; Krantz *et al.*, 1949; and others). The results have followed a rather typical pattern.

Phosphate fertilizers are most frequently applied at the time of planting. These applications are usually localized in the proximity of the seeds or young plants. Under conditions of inadequate supplies of soil phosphorus such applications increase both growth and total phosphorus absorption. In the early stages of growth, seedlings absorb phosphorus at a faster rate from the fertilizer than from the soil, the net result being that in young plants a high proportion of the total phosphorus absorbed is that derived from the fertilizer. As the plants develop, the enlarging root system continuously increases the amount of soil phosphorus which is accessible. This increases the rate of absorption of soil phosphorus as compared with that of fertilizer phosphorus, and mature plants characteristically have a lower per cent of phosphorus in the crop derived from the fertilizer than at the earlier stages of growth.

The data on the absorption of phosphorus by corn (Table I) illustrate the effect of phosphorus fertilization on absorption rates. The comparison is between no phosphorus and a 60 pound per acre rate of P_2O_5 as superphosphate. The largest difference in yield was noted at the 60-day sampling period. At final harvest there was no significant difference in grain yields, although the fertilizer application increased the total phosphorus absorption. The greatest relative increase in total phosphorus absorption resulting from fertilization was at the first sampling. During the period 0 to 30 days more phosphorus entered the plant from the fertilizer than from the soil, but the total amount involved was small. From then on the total absorption rate rapidly increased and the contribution of the fertilizer phosphorus decreased. The effect of the

TABLE I

RATE OF ABSORPTION OF SOIL AND FERTILIZER PHOSPHORUS BY CORN[a]

Age at sampling, days	P_2O_5 treatment					
	None	60 pounds	None	60 pounds	60 pounds	60 pounds
	Yield, pounds/acre		Total P_2O_5 absorbed, pounds/acre		Soil P_2O_5 absorbed, pounds/acre	Fertilizer P_2O_5 absorbed, pounds/acre
30	11.3	13.4	0.04	0.07	0.03	0.04
60	337	459	1.2	1.6	1.1	0.5
90	6760	7315	8.1	9.5	8.4	1.1

[a] Data of Stanford and Nelson (1949).

absorption rate of seedlings on the functioning of the plant and on the ultimate yield has not been fully evaluated.

III. The Soil as a Supplier of Phosphorus

Growth rate, yield, or quality of crops may or may not be limited by the rate at which the plants absorb phosphorus from the soil. The supply of phosphorus in the soil is one factor that determines this absorption rate. Therefore it is of interest to define the potentialities of a soil as a supplier of phosphorus.

The soil and the plant comprise a heterogeneous system. It is a dynamic, ever-changing system. The roots of seedling plants grow, bringing an increasing volume of soil into the system. The soil itself undergoes cycles of wetting and drying. There are also continuous changes being brought about by microbiological activity. In assessing the soil as a supplier of phosphorus the plant can hardly be looked upon as a passive agent. That is, to a degree the plant influences the capacity of a soil to supply phosphorus. As yet, our knowledge regarding the various processes and mechanisms and the interactions involved is incomplete.

From a practical standpoint the interest in the capacity of the soil to supply phosphorus lies in the economic implications. A common question is: "What will be the consequences of changing the present supply?" Experiments have been conducted for the purpose of determining the changes brought about both in the phosphorus content of plants and in yields when the soil phosphorus supply is altered. From these experimental measurements it is possible to make certain deductions regarding the soil as a supplier of phosphorus.

1. Plant Growth as Influenced by Soil Phosphorus Supply

When the soil phosphorus supply is a limiting factor in plant growth increments of phosphate fertilizer added to the soil will result in increased yields of dry matter. Growth curves constructed from data of both field and greenhouse experiments have shown plant growth to be a function of nutrient supply. Both Mitscherlich (1912, 1930) and Spillman (1921, 1933) have suggested expressions for this relationship based on the assumption that the change in yield per added unit of applied fertilizer depends upon the proximity to maximum yields.

This relationship can be expressed mathematically as:

$$Y = M - AR^X$$

where Y = yield obtained when X units of nutrient are applied as a fertilizer.

X = number of units of nutrient applied.

M = limit approached by Y as X is increased (theoretical maximum yield).

A = theoretical maximum *increase* in yield obtained by increasing X indefinitely.

R = constant.

The curve which represents this expression is shown in Fig. 2, curve 1. An estimate of the phosphorus supply of the original soil is obtained by extrapolation of this curve to the point where it intersects the X

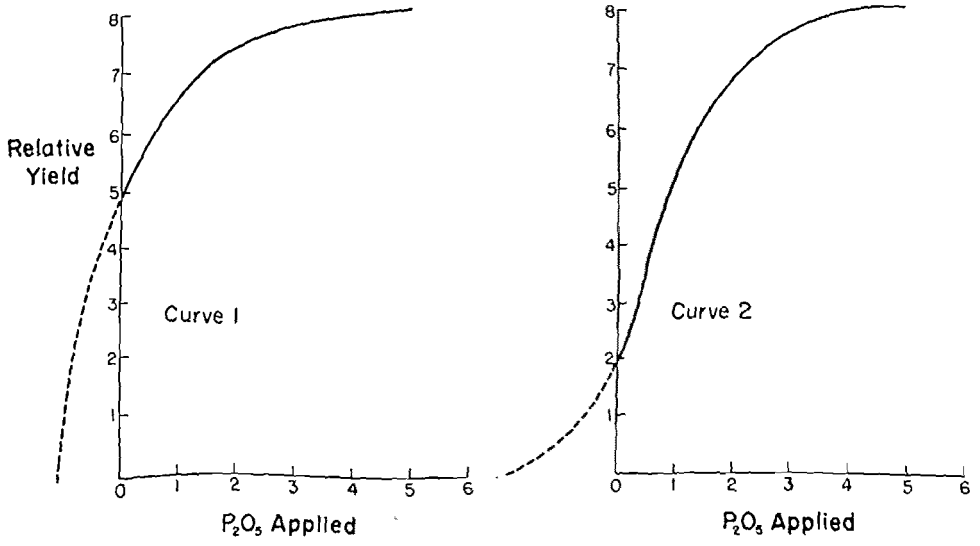


FIG. 2. Schematic representation of growth curves.

axis. The number of units between this point of intersection and the Y axis is known as the *b* value. This *b* value gives the amount of soil phosphorus in terms of equivalent amounts of fertilizer phosphorus. Certain of the experimental evidence indicates that growth response curves are sigmoid in shape (see curve 2 in Fig. 2). Extremely phosphorus-deficient soils are required to demonstrate this sigmoid shape. Ordinarily this difference is of little consequence, since the upper parts of the two curves are similar. However, if an extrapolation is made, such as required to measure the *b* value, then serious differences would occur, depending upon the nature of the assumed growth curve.

Both Mitscherlich (1930) and Spillman (1933) recognized that the level of other nutrients might affect yield interpretations, and they attempted to take into account the level of the three major nutrients, nitrogen, phosphorus, and potassium. Interactions between nutrient supply and environment also influence the growth response (Russell, 1950).

The growth curves show that the magnitude of yield change resulting from a change in soil phosphorus supply depends upon the maximum yield. Thus, any factor affecting the maximum yield will alter conclusions drawn with regard to the soil phosphorus supply. Steinbjerg (1952) has discussed the factors which determine the shape and position of the yield curve and has grouped them under the following four headings:

1. Soil factors.
2. Climate factors.
3. Crop.
4. The stage of development of the harvested crop.

It is apparent, therefore, that the consequences, in terms of yield, of altering the phosphorus supply of the soil by adding different amounts and/or kinds of phosphorus fertilizers may be predicted with accuracy only under highly specialized conditions, and that the phosphorus supply of a soil, although real, may have a wide range of apparent values.

2. Plant Composition as Influenced by Soil Phosphorus Supply

Altering the phosphorus supply of a soil can be shown to cause rather systematic changes in the total amount of phosphorus absorbed and the phosphorus content (percentage) of crops. These changes embrace an interaction with yield or growth. This influence of change in the soil phosphorus supply can be illustrated if the crops grown to produce the yield curve previously discussed are analyzed for total phosphorus and these data plotted against the increased phosphorus additions and yield as shown in Fig. 3.

Depending upon phosphorus level in the original soil, an increase in the soil phosphorus supply may result in increasing, decreasing, or leaving the percentage of phosphorus in the plant unchanged. However, under conditions where increasing the soil phosphorus supply results in no, or relatively small, growth changes, an increase in supply usually is accompanied by an increase in both the percentage of phosphorus and in the total phosphorus uptake.

The same set of factors that have been shown to determine the shape and position of the yield curves will also influence phosphorus content and uptake. Among these are supply of the other nutrients, plant species, age and part of plant, soil moisture, and temperature and sun-

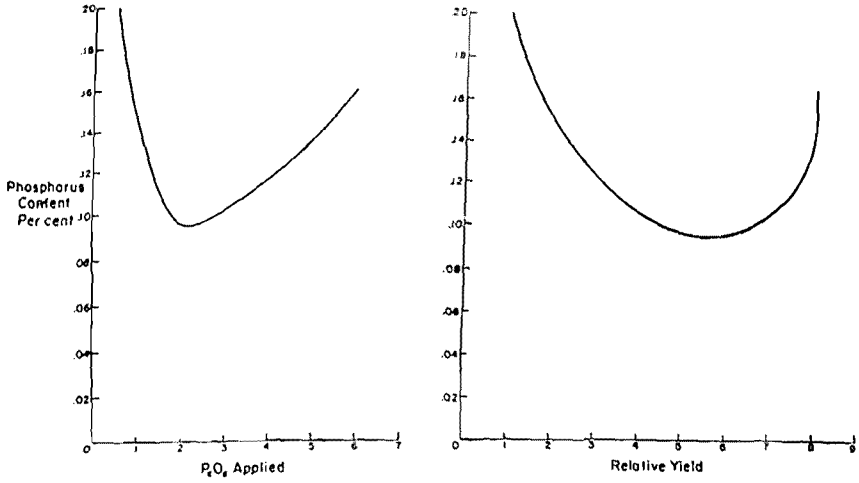


FIG. 3. Schematic representation of the changes in phosphorus content of plants.

light during growth. Early attempts to use plant composition as a criterion of soil nutrient supply proved impractical (Hall, 1905). However, more recent investigations have shown that, for local areas of similar soils and climate, analysis of a particular plant part at a definite stage of growth will give useful information regarding the changing phosphorus supply of soils (Macy, 1936; Thomas, 1945; Ulrich, 1948; Jakobsen, 1952; and others).

3. *Relative Absorption of Soil and Fertilizer Phosphorus*

Reports by Fried and Dean (1952) and Larsen (1952) suggest that the results of radiochemical analyses of plants grown on soils which received applications of fertilizers containing P^{32} may be used to calculate the phosphorus supply of the original soil. The hypothesis suggested by Fried and Dean (1952) assumed that a plant presented with two

sources of phosphorus, namely the soil and the fertilizer, will absorb phosphorus from each in direct proportion to the amounts of these respective supplies. This results in the following relationship between the magnitude of the two sources and the proportion of the phosphorus in the plant that is derived from the fertilizer:

$$A = \frac{B(1 - y)}{y}$$

where A = the amount of the soil phosphorus supply.
B = the amount of the fertilizer phosphorus supply.
y = fraction of the phosphorus in the plant derived from the fertilizer.

Experimentally this relationship has been used in the following way: Known amounts of phosphatic fertilizer labeled with P^{32} at a known specific activity are mixed uniformly with a soil and the desired crop grown. The plants are analyzed and the specific activity of their phosphorus determined. The ratio of the specific activity of the plant material to that of the original fertilizer is taken to be y, the fraction of the phosphorus in the plant derived from the fertilizer. Since B is known, A may then be calculated from the above equation. This quantity of soil phosphorus is in terms of the fertilizer added to the soil. In this respect the A value is identical to the b value of Mitscherlich. A parallelism exists between the method as described and the well-known technique of analysis by isotopic dilution. This application has been discussed by Larsen (1952).

Figure 4 gives a series of results for two soils which differ in phosphorus fertility. These data were selected from a greenhouse experiment with millet as a test crop. The phosphorus fertilizer, monocalcium phosphate containing P^{32}, at rates of 0, 40, 80, and 160 pounds P_2O_5 per acre, was applied by mixing well with all the soil in each pot. In this experiment the same plant samples were used to make all measurements: namely, the yield, the phosphorus percentage, and the amount of total soil and fertilizer phosphorus in the harvested crop.

The yield curves are as expected for soils of low and medium phosphorus fertility. The b values obtained by extrapolation indicate that the original soils contained 9 and 60 pounds P_2O_5 per acre in terms of the monocalcium phosphate which was applied at planting. The curve representing the change in total phosphorus percentage is U-shaped for one soil and an ascending straight line for the other. Amounts of total phosphorus and fertilizer phosphorus absorbed increased with increasing applications of fertilizer. Except for the displacement between the 0- and 40-pound rates there is little influence of rates on the amounts of

ANGRAU
Central Library
Rajendranagar
G790

soil phosphorus absorbed. Possibly the displacement can be accounted for by the assumption that the distribution of the total phosphorus absorbed between roots and shoots changes when fertilizers are added to deficient soils.

The total phosphorus absorbed is actually the yield of phosphorus. As such, it would appear logical to extrapolate the yield of phosphorus curves until they intersect the X axis and obtain values similar to the Mitscherlich b value. If the data for the two soils illustrated in Fig. 4

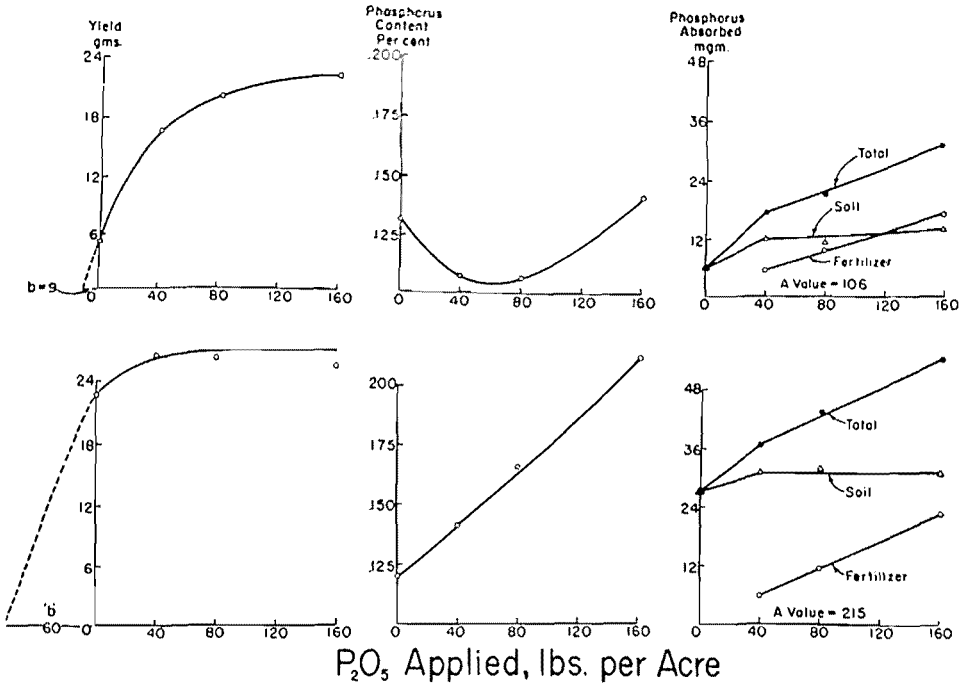


FIG. 4. Yield, phosphorus content, and absorption as influenced by fertilizer applications on two soils.

are considered, and the straight lines formed when the total phosphorus absorbed from the 40-, 80-, and 160-pound rates are drawn, extrapolation of these lines give estimates of the soil phosphorus supply closely approximating the A value. The significance of this observation is currently under investigation.

The A value suggests the soil phosphorus supplies to be considerably greater than as estimated by the b value method.

The curves in Fig. 4 are not reproducible except under the most exact experimental conditions. In other words, depending upon the circumstances it is possible to draw a variety of conclusions regarding the absolute magnitude of the soil phosphorus supply and the changes that

will be brought about by addition of varying amounts or different kinds of phosphatic fertilizers.

The *A* value which is calculated from the ratio of soil phosphorus absorbed to fertilizer phosphorus absorbed, on the other hand, is not necessarily appreciably altered by the same factors that change the growth and the phosphorus-absorption pattern. This value is dependent upon the amounts of the two supplies of phosphorus: namely, the soil and the fertilizer. Therefore, the method is equally applicable for measuring either the soil phosphorus or the fertilizer phosphorus in terms of the other. Experimentally it has not been possible to measure the *A* value in terms of an absolute chemical compound. There remains the necessity of developing a technique whereby fertilizers added to soils will remain unaltered and at the same time be as accessible to the plants as the soil phosphorus. Experiments to attain this ideal are still in progress.

IV. The Phosphorus-Absorption Processes

As matters presently stand there is no generally accepted composite picture of the processes taking place during phosphorus absorption by plants. Marked progress has been made in the understanding of several phases of the overall process. Recent reviews (Overstreet and Jacobson, 1952; Robertson, 1951) have shown the development in the understanding of the mechanisms of ion absorption by roots. Chapters III, IV, and V in this monograph deal with the chemistry of soil phosphorus and its release. These specific aspects are not repeated here. The present discussion is confined to the soil-plant system as a unit.

Phosphorus absorption entails the transfer of phosphate ions from the soil to the roots and into the plant. A generalized model of the system is given in Fig. 5. This system includes the soil and root surfaces with their associated phosphate ions in equilibrium with an intermicellar liquid phase. Although not illustrated, there is in all probability a diffuse double layer of ions associated with both the soil and root surfaces. The predominant charge of both surfaces is negative. The illustration shows a higher concentration of phosphate ions at some distance from the negative surfaces than in the immediate vicinity. Such a distribution is in accordance with the Donnan principle.

Studies by McAuliffe *et al.* (1947), Wiklander (1950), and Olsen (1952) have indicated that some of the phosphate ions associated with the soil surfaces are exchangeable with phosphate ions in solution. Wiklander (1950) and Barbier and Tyskiewicz (1952) have shown an exchange between these surface exchangeable phosphate ions and others of the solid phase.

In a recent review Overstreet and Dean (1951) discussed the evidence for an exchange between phosphate ions associated with the root surfaces and those in the surrounding aqueous solution. Phosphate ions have been shown to migrate from root surfaces to the clay surfaces.

Inasmuch as the absorption process by roots involves the transfer of phosphate ions into the root tissue and out of the system, the system as pictured is not in equilibrium. There would be a tendency toward a migration to the root. However, this does not preclude that the reverse

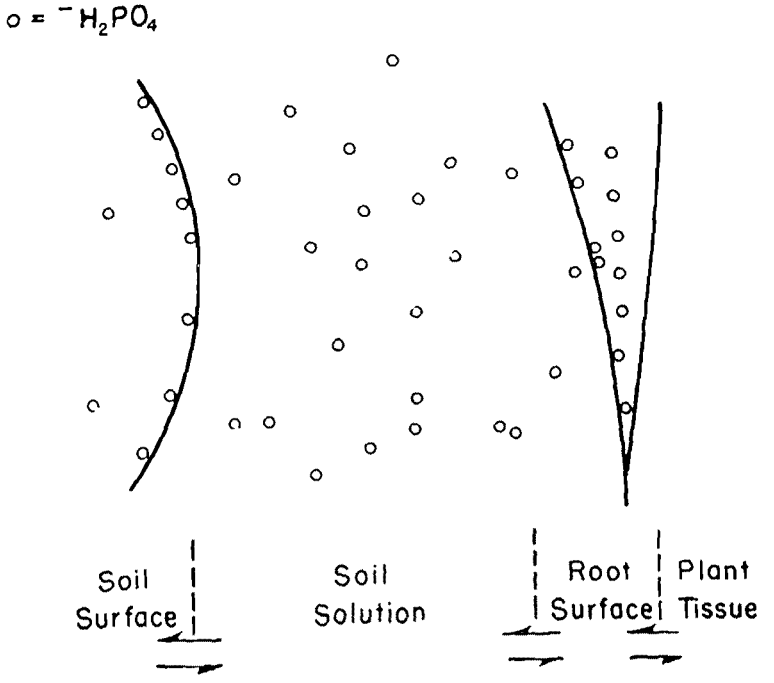


FIG. 5. A model of the phosphorus-absorption processes.

may take place. For example, Dean and Rubins (1945) showed that when barley roots grown in the high-phosphorus environment of a nutrient solution are transferred to a clay suspension there is a loss of phosphorus from the roots to the clay.

This discussion of the phosphorus absorption processes from soil has been grossly over-simplified. Soil phosphate ions are not independent of the other ion species. These salt effects have been discussed by Mattson *et al.* (1949, 1950). Such theoretical considerations point out that phosphorus absorption by plants from soils depends not only on the nature and concentration of cations and anions but upon the relative properties of opposing soil and root surfaces.

The root tips of plants undergo growth; during growth new surfaces are being formed. Since the soil particles are heterogeneous and the moisture films are largely discontinuous, each new root-soil system developed as the result of growth may be different. On the other hand, the aging of root tissues is continuously bringing about changes. Thus, the over-all absorption of phosphorus from soils is the integration or net effect of many isolated root-soil systems.

The minimum phosphorus concentration necessary for optimum growth has been determined for a variety of crops (Parker, 1927; Tidmore, 1930; Sommer, 1936; and Houghland, 1947). These studies were undertaken in nutrient solutions and the phosphorus concentrations were maintained as nearly constant as possible. The results have shown growth to be impeded in solutions of 0.1 p.p.m. P or less. On the other hand, crops appear to grow normally on soils where the soil solution concentration as measured by displacement methods is less than 0.1 p.p.m. The apparent discrepancy was discussed by Parker (1927) on the basis of one or more of the following assumptions.

1. The displaced solution is not the true soil solution.
2. The plant roots exert a solvent action on the soil particles and thus bring more phosphorus into solution and produce a higher concentration at the absorbing surfaces.
3. As a result of a Donnan equilibrium, there is a higher concentration of phosphorus in the solution at the surface of the soil particles than in the displaced soil solution.

At that date the presumptive evidence appeared to favor the second assumption: namely, that there was a contact effect between plant roots and soil particles.

The discussion describing the root-soil system has pointed to certain lines of evidence which indicate that the phosphorus content of the displaced soil solution does not adequately define the environment of the root-soil system as it pertains to phosphorus absorption. The phosphorus content of the intermicellar liquid probably is not uniform throughout the soil. There is no information, however, indicating the distribution of these concentration gradients. There is certain limited evidence indicating that the soil solution is a necessary and integral part of the system. Experiments by Hunter and Kelley (1946) indicated that phosphate ions are not absorbed from dry soils, Volk (1947) concluded that cations but not anions may be absorbed from dry soils, and Haddock (1952) has shown that phosphorus absorption can be altered by irrigation practice.

The contention that plant roots exert an influence on soil particles as a result of contact proximity and that this in turn increases the ab-

sorption rate is still unanswered. The evidence for such a phenomenon is presumptive. In this connection, Thomas (1930) prepared a review dealing with the feeding power of plants. Several of the theories propose that plants give off CO_2 and possibly other acidic compounds which increase the amounts of phosphorus liberated from soil surfaces (Haas, 1916; Hall, 1906; Stoklasa and Ernest, 1908; and others). Others have proposed a similar role for soil microorganisms. Gerretsen (1948) and Pikovskaya (1948) compared the phosphorus uptake by plants growing in sterile and nonsterile cultures and showed more phosphorus to be absorbed from basic calcium phosphates in the presence of microorganisms. The suggestion has also been made that soil microorganisms produce organic acids which form complex ions with iron and aluminum, thus leading to increased utilization of soil phosphorus by plants (Dalton *et al.*, 1952). It would appear not improbable that cellular excretions do influence the phosphorus-absorption process.

Both Tschirikow (1914) and Truog (1916) have emphasized the relation between the calcium uptake by plants and the absorption of phosphate from basic calcium phosphates. As a result of observation on associations of different plant species Domonotovich (1924) re-emphasized this theory.

A "contact exchange theory" has been proposed by Jenny and coworkers (1939, 1939a). They were able to show that, with certain clay or soil suspension containing Na^+, K^+, or Rb^+, the rates of absorption of the ions by barley roots were greater than from corresponding salt solutions. Experiments to date have not shown a corresponding influence of clay particles on anion absorption. The experiments by Dean and Rubins (1945) failed to show a greater phosphorus absorption in the presence of clay suspensions containing fixed phosphorus.

Much of the evidence supporting a contact effect is contained in the studies on the utilization of basic calcium phosphates by crops, the classic example being the differential feeding of plants on rock phosphate. As early as 1898, Merrill reported that the influence of rock phosphate on the growth of plants varied with the species. In general, it has been shown that the most efficient users of rock phosphate are lupines, buckwheat, sweet clover, mustard, swiss chard, vetch, and to a lesser extent alfalfa, peas, rape, and cabbage. The following crops are considered to be very poor users of rock phosphate: cotton, cowpeas, bur clover, rice, oats, barley, millet, rye, and wheat.

Most experiments comparing the feeding power of different plants do not permit distinguishing whether the observed differences are due to the extent of the root surfaces involved or to a specific property of these root surfaces. An experiment conducted recently at Beltsville was

PAU CENTRAL LIBRARY
Acc: No: 4790
97.9.86

designed to measure the importance of specific properties of the root surface. The phosphorus supply of several soils was labeled by the addition of superphosphate containing P^{32}. Then a supply of rock phosphate was introduced and mixed throughout. These soils were used to grow a variety of plant species in pot culture and the specific activity of these plants was subsequently determined. Since under these conditions the phosphorus of the soil and that of the rock phosphate are equally accessible to the root system any difference in the specific activity of the plants grown is attributable to differences in the properties of the root surfaces of the various species tested and not to the extent of the root systems. The results of this experiment showed such differences to occur and that the relative feeding powers of the species tested were similar to the findings previously reported in the literature.

References

Barbier, G., and Tyskiewicz, F. 1952. Mobilité des ion phosphoriques "fixes" dans le sol étudiée au moyen de P^{32}. *Trans. Intern. Soc. Soil Sci., Joint Meeting of* Comm. II and IV, Dublin. **2**: (In press).

Beeson, K. C. 1941. The mineral composition of crops with particular reference to the soils in which they were grown. A review and compilation. *U.S. Dept. Agr. Misc. Pub.* **369**.

Dalton, J. D., Russell, G. C., and Sieling, D. H. 1952. Effect of organic matter on phosphate availability. *Soil Sci.* **73**: 173–181.

Dean, L. A., and Rubins, E. J. 1945. Absorption by plants of phosphorus from a clay-water system: Methods and ensuing observation. *Soil Sci.* **59**: 437–448.

Domontovich, M. 1924. Phosphates in vegetation experiments. *Trans. Sci. Inst. Fertilizers Insectofungicides* (*U.S.S.R.*) **12**: 141–175.

Fried, M., and Dean, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

Gerretsen, F. C. 1948. The influence of microorganisms on the phosphate intake by the plant. *Plant and Soil* **1**: 51–81.

Grizzard, A. L., Davies, H. R., and Kangas, L. R. 1942. The time and rate of nutrient absorption by flue cured tobacco. *J. Am. Soc. Agron.* **34**: 327–339.

Haas, A. R. C. 1916. The excretion of acids by roots. *Proc. Nat. Acad. Sci. U.S.* **2**: 561–566.

Haddock, J. L. 1952. The influence of soil moisture conditions on the uptake of phosphorus from calcareous soils by sugar beets. *Soil Sci. Soc. Amer. Proc.* **16**: 235–238.

Hall, A. D. 1905. The analysis of the soil by means of the plant. *J. Agr. Sci.* **1**: 65–89.

Hall, A. D. 1906. The solvent action of roots upon the soil particles. *Sci. Prog.* **1**: 51–57.

Hawkins, A. 1946. Rate of absorption and translocation of mineral nutrients by potatoes in Aroostook County, Maine, and their relation to fertilizer practices. *J. Am. Soc. Agron.* **38**: 667–681.

Hester, J. B. 1938. The absorption of nutrients by the tomato plant at different stages of growth. *Proc. Am. Soc. Hort. Sci.* **36**: 720–722.

HOUGHLAND, G. V. C. 1947. Minimum phosphate requirement of potato plants grown in solution cultures. *J. Agr. Research* **75**: 1–18.

HUNTER, A. S., and KELLEY, O. J. 1946. The extension of plant roots into dry soil. *Plant Physiol.* **21**: 445–451.

JACOB, W. C., VAN MIDDELEM, C. H., NELSON, W. L., WELCH, C. D., and HALL, N. S. 1949. Utilization of phosphorus by potatoes. *Soil Sci.* **68**: 113–120.

JAKOBSEN, S. T. 1952. Om den S-formede udbyttekurves betydning for vur der ingen af den kemiske planteanalyse. *Horticultura (Denmark)* **6**: 12–15.

JENNY, H., and OVERSTREET, R. 1939. Cation interchange between plant roots and soil colloids. *Soil Sci.* **47**: 257–272.

JENNY, H., OVERSTREET, R., and AYRES, A. D. 1939a. Contact depletion of barley roots as revealed by radioactive indicators. *Soil Sci.* **48**: 9–24.

KRANTZ, B. A., NELSON, W. L., WELCH, C. D., and HALL, N. S. 1949. A comparison of phosphorus utilization by crops. *Soil Sci.* **68**: 171–177.

LARSEN, S. 1952. The use of P^{32} in studies on the uptake of phosphorus by plants. *Plant and Soil* **4**: 1–10.

MCAULIFFE, C. D., HALL, N. S., DEAN, L. A., and HENDRICKS, S. B. 1947. Exchange reactions between phosphates and soil: Hydroxylic surfaces of soil minerals. *Soil Sci. Soc. Amer. Proc.* **12**: 119–123.

MACY, P. 1936. The quantitative mineral nutrient requirements of plants. *Plant Physiol.* **11**: 749–764.

MATTSON, S., ERIKSSON, E., VAHTRAS, K., and WILLIAMS, E. G. 1949. Phosphate relationships of soil and plant: I. Membrane equilibria and phosphate uptake. *Ann. Roy. Agr. Coll. Sweden* **16**: 457–484.

MATTSON, S., WILLIAMS, F. G., ERIKSSON, E., and VAHTRAS, K. 1950. Phosphate relations of soil and plant: II. Soil-soil solution equilibria and phosphate solubility. *Ann. Roy. Agr. Coll. Sweden* **17**: 64–91.

MERRILL, L. H. 1898. Box experiments with phosphoric acid from different sources. *Ann. Report Maine Agr. Expt. Sta.* pp. 64–74.

MITSCHERLICH, E. A. 1912. Zum Gesetz vom Minimum. Eine Antwort an Th. Pfeiffer und seine Mitanbeiter. *Landw. Vers. Sta.* **77**: 413–428.

MITSCHERLICH, E. A. 1930. Eine Bestimmung des Düngebedürfnisses des Bodens. Verlagsbuchhandlung Paul Parey, Berlin.

NELSON, W. L., KRANTZ, B. A., COLWELL, W. E., WOLTZ, W. G., HAWKINS, A., DEAN, L. A., MACKENZIE, A. J., and RUBINS, E. J. 1947. Application of radioactive tracer technique to studies of phosphate fertilizer utilization by crops: II. Field experiments. *Soil Sci. Soc. Amer. Proc.* **12**: 113–118.

OLSEN, S. R. 1952. Measurement of surface phosphate on hydroxylapatite and phosphate rock with radiophosphorus. *J. Phys. Chem.* **56**: 630–632.

OLSON, L. C., and BLEDSOE, R. P. 1942. The chemical composition of the cotton plant and the uptake of nutrients at different stages of growth. *Georgia Agr. Expt. Sta. Bull.* **222**.

OVERSTREET, R., and DEAN, L. A. 1951. The availability of soil anions. *In* Mineral Nutrition of Plants, pp. 79–105. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

OVERSTREET, R., and JACOBSON, L. 1952. Mechanism of ion absorption by roots. *Ann. Rev. Plant Physiol.* **3**: 189–206.

PARKER, F. W. 1924. Carbon dioxide production of plant roots as a factor in the feeding power of plants. *Soil Sci.* **17**: 229–247.

PARKER, F. W. 1927. Soil phosphorus studies: III. Plant growth and the absorption

of phosphorus from culture solutions of different phosphate concentrations. *Soil Sci.* **24**: 129–146.

PARKER, F. W. 1927a. Recent studies on the phosphate content of the soil solution and its relation to the phosphorus nutrition of the plant. *Trans. Intern. Congr. Soil Sci.* **2**: 384–395.

PIKOVSKAYA, R. I. 1948. Mobilization of phosphate in soil in relation to vital activities of certain species of bacteria. *Microbiology (U.S.S.R.)* **17**: 362–370.

REMY, T. 1938. Fertilization in its relationship to the course of nutrient absorption by plants. *Soil Sci.* **46**: 187–209.

ROBERTSON, R. N. 1951. Mechanism of absorption and transport of inorganic nutrients in plants. *Ann. Rev. Plant Physiol.* **2**: 1–25.

RUSSELL, E. J. 1950. Soil Conditions and Plant Growth. 8th Ed., 635 pp. Longmans, Green and Co., New York.

SOMMER, A. L. 1936. The relationship of the phosphate concentrations of solution cultures to the type and size of root systems and the time of maturity of certain plants. *J. Agr. Research* **52**: 133–148.

SPILLMAN, W. J. 1921. A plan for the conduct of fertilizer experiments. *J. Am. Soc. Agron.* **13**: 304–310.

SPILLMAN, W. J. 1933. Use of the exponential yield curve in fertilizer experiments. *U. S. Dept. Agr. Tech. Bull.* **348**.

SPINKS, J. W. T., and BARBER, S. A. 1947. Study of fertilizer uptake using radioactive phosphorus. *Sci. Agr.* **27**: 145–156.

STANFORD, G., and NELSON, L. B. 1949. Utilization of phosphorus as affected by placement: I. Corn in Iowa. *Soil Sci.* **68**: 129–135.

STEINBJERG, F. 1952. Verification of chemical soil and plant analyses: General considerations. *Trans. Intern. Soc. Soil Sci. Commissions II and IV Dublin* **1**: 309–322.

STOKLASA, J., and ERNEST, A. 1908. Beiträge zur Lösung der Frage der chemischen Natur des Wurzelsekretes. *Jahrb. wiss. Botan.* **46**: 55–102.

THOMAS, W. 1930. The feeding power of plants. *Plant Physiol.* **5**: 443–489.

THOMAS, W. 1945. Present status of diagnosis of mineral requirements of plants by means of leaf analysis. *Soil Sci.* **59**: 353–374.

TIDMORE, J. W. 1930. Phosphate studies in solution cultures. *Soil Sci.* **30**: 13–31.

TRUOG, E. 1916. The utilization of phosphate by agricultural crops including a new theory regarding the feeding power of plants. *Wisconsin Agr. Expt. Sta. Research Bull.* **41**.

TSCHIRIKOW, T. W. 1914. Zur Frage über die lösende Wirkung der Wurzeln. *Zhur. Opyt. Agron.* **15**: 54–65.

ULRICH, A. 1948. Diagnostic Techniques for Crops and Soils. VI. Plant analysis—methods and interpretation of results, pp. 157–198. American Potash Institute. Washington, D. C.

VOLK, G. M. 1947. Significance of moisture translocation from zones of low moisture tension to zones of high moisture tension by plant roots. *J. Am. Soc. Agron.* **39**: 93–106.

WIKLANDER, L. 1950. Kinetics of phosphate exchange in soils. *Ann. Roy. Agr. Coll. Sweden* **17**: 407–424.

WILLIAMS, R. F. 1948. The effects of phosphorus supply on the rates of intake of phosphorus and nitrogen and upon certain aspects of phosphorus metabolism in gramineous plants. *Australian J. Sci. Research* **B1**: 333–361.

WOLTZ, W. G., HALL, N. S., and COLWELL, W. E. 1949. Utilization of phosphorus by tobacco. *Soil Sci.* **68**: 121–128.

CHAPTER III

Inorganic Phosphorus in Acid and Neutral Soils

L. T. KURTZ

I. Introduction

1. General

Emphasis on the chemistry of phosphorus in soils arises from its importance as a plant nutrient and from the influence which the chemical form and reactions of this element have in its utilization for crop production.

Knowledge of the chemistry of phosphorus in soils is a requirement for knowledge of its utilization by plants, and explanations of soil-plant relations will be clear only when the forms and properties of soil phosphorus are known.

The realization that a knowledge of the chemical behavior of phosphorus in soils is of agronomic value has prompted many studies of the behavior of phosphorus in soil systems entirely apart from the role of soil phosphorus in plant nutrition. Attempts to fractionate soil phosphorus and to learn the chemical nature of the fractions have been and will continue to be subjects of fruitful research. Literature reporting studies to determine the forms which added phosphorus assumes in soils is extensive and frequently confusing. Research on soil phosphorus is complicated by the fact that each of the phosphate ions forms a multitude of compounds of low solubility and often of highly variable composition.

The object of this chapter is to present something of the chemistry of phosphorus in neutral and acid soils as it has been reported and understood to date. The literature of this subject is extensive and even a mention of all of the pertinent papers is impossible. The writer hopes at best to suggest references bearing on the chief forms and reactions of phosphorus in soils.

2. Review References on Chemistry of Phosphates in Soils

Several articles summarizing the literature on soil phosphorus and the reactions of phosphorus in soils have appeared. Among the more recent were reviews by Wild (1950a) and Dean (1949) on the reten-

tion and fixation of phosphorus in soils. An article of broader scope by Pierre (1948) reported on the organic forms as well as on the inorganic forms of phosphorus in soils. A summary of phosphorus research prepared by the National Phosphorus Research Work Group (1950) contained bibliographies on many phases of phosphorus research for the period 1935 to 1950. A review of the literature on phosphate fixation was also made earlier by Midgely (1940). An extensive review was also published still earlier by Weiser (1933) in connection with his work on phosphate fixation.

3. *Historical References on Chemistry of Phosphates in Soils*

The reactions of phosphates in soils have been studied intensively and almost continuously since chemistry began to play its role in soil science. Way (1850), who was among the first to observe cation exchange, also observed that phosphates were taken from solution by soils. Even prior to the publication of Way's quantitative data, Liebig (1840), according to Wild (1950a), was aware of phosphate retention by soils. Certainly in his later writings Liebig (1863) discussed absorption by soils at considerable length and apparently considered this form of plant nutrients very important in crop production. In this same period, Daubney (1845) studied methods of extracting "available" phosphorus from the soils and reported phosphorus fertility studies. Research on soil phosphorus has apparently continued since that time and numerous references appeared during the last half of the nineteenth century. Work of Van Bemmelen (1888), who studied "absorption" by soils, and Dyer's (1894) studies of extractants for soil phosphorus are only two examples of noteworthy contributions of this period.

Apparently few reports of work in the United States appeared in print until after 1900. A series of lectures given by Dyer (1902) in this country were published in 1902 as a bulletin of the Office of the Experiment Station. These lectures had been presented before the Association of American Agricultural Colleges and Experiment Stations and discussed the fertility work at Rothamsted with considerable emphasis upon chemical analysis as a method to predict crop responses to phosphate fertilizers. Active research on soil phosphorus was apparently under way in the Bureau of Soils during this period, since several publications, among which was a bulletin on "absorption of phosphates and potassium by soils" by Schreiner and Failyer (1906), appeared in the next few years. Research papers by Fraps (1906) and Stoddart (1909) and a discussion of phosphate reactions by King (1914) serve as examples of work done in this country in the early part of the present century. Fraps' paper is of especial interest, since he recognized the

difference between phosphorus forms present in "calcareous" soils as compared to "siliceous" soils. Fraps also discussed the differences between "chemical," "positional," "weathering," and "physiological availabilities," using the terms approximately as they are used today.

II. Forms and Amounts of Native Phosphorus in Soils

1. Total Phosphorus

Phosphorus in the lithosphere has been placed at 0.28 per cent P_2O_5 by Clarke (1920) and is considerably higher than the average figure of 0.09 per cent given for representative mineral soils of the United States by Robinson *et al.* (1917), who found the P_2O_5 percentages to vary in these soils from 0.03 to 0.22 per cent. Bryan (1933) reported analyses of Florida soils and a P_2O_5 percentage of 0.012 in St. Lucie sand. Obviously the total phosphorus in soils may vary over a wide range depending on organic matter content, parent material, and degree of weathering. Mooers (1906) reported soils with a content of P_2O_5 greater than 1 per cent and even higher analyses have been given by Peter and Averitt (1906) for soils derived from phosphatic parent material. Generalized maps showing the phosphorus content of soils of this country have been prepared by an Agriculture Committee on National Policy (1945).

Except for research studies, determinations of total phosphorus in soils have been made rarely in recent years, since total phosphorus is generally recognized as of little value in assessing the phosphorus fertility of a soil. Attempts to use total phosphorus determinations for this purpose were made and many total analyses were run. This concept was probably carried farthest by Hopkins (1910) and his associates at Illinois, where total phosphorus was determined on literally thousands of soil samples. Many of the data were published in the contemporary soil survey reports of the Illinois Station, and comparisons of total phosphorus in soils from points widely scattered over the world were made by Hopkins.

2. Organic Phosphorus in Soils

Soil phosphorus is usually considered primarily under two classes, organic and inorganic, each of which must be further subdivided. Present knowledge and reported data are both inadequate to make a completely satisfactory classification under either class. A multitude of compounds both organic and inorganic in nature could conceivably exist under soil conditions, and the properties of some of these have been studied extensively. The organic forms are dealt with in Chapter V and will not be discussed here. It must be mentioned, however,

that the proportion of organic phosphorus in soils may be high and that the bulk of the soil phosphorus in many agriculture soils is in the organic form.

3. *Inorganic Phosphorus in Soils*

a. Water-Soluble Inorganic Phosphorus. Investigations to determine the concentration of phosphorus in soil solutions or in water extracts of soils have shown that this form is extremely small. Burd and Martin (1923) and Pierre and Parker (1927) have shown that these concentrations are of the same order and are ordinarily much less than one part per million. In some of the productive soils studied, Parker and Tidmore (1926) found that the water extracts and displaced soil solutions were more dilute in phosphorus than the minimum concentrations necessary for good plant growth in nutrient solution.

Water-soluble inorganic phosphorus in soils is not a discrete form of some soluble phosphate salt dissolved in the soil solution. Ordinarily water-soluble phosphate is more accurately regarded as a concentration in equilibrium either with forms adsorbed on colloidal surfaces or with a combination of phosphate compounds of low solubility. The evidence on these alternatives will be considered later.

b. "Acid-Soluble" Forms of Phosphorus in Soils. A large portion of inorganic soil phosphorus is soluble in acid and different concentrations of a number of acids have been used in phosphorus extraction studies. Although acids of specified strength do not make clean separations of specific forms of phosphorus, some selectivity can be obtained by varying the concentration, the time of reaction, and the anion of the acid used.

(1) Soil phosphorus soluble in strong, concentrated acids. Prolonged digestions with concentrated mineral acids are considered to remove the bulk but not all the phosphorus from soils. McLean (1936) studied the ability of strong acids, nitric, hydrochloric, and sulfuric, and found that practically the same amount of phosphorus was removed in different digestion periods from 1 to 48 hours. His conclusion that such extractions remove a definite phosphorus fraction is partially supported by Piper (1947), who, in summarizing methods for hydrochloric acid extracts, states that constant-boiling hydrochloric acid gives approximately the same results as concentrated hydrochloric acid and that approximately as much phosphorus is dissolved in 1 hour as in 48 hours.

Digestion of soils in strong hydrochloric acid was formerly believed to separate the "weathered" from the "unweathered" minerals and to give an estimate of the "total source" of the respective mineral nutrients.

Prolonged treatment with strong acids can be expected to dissolve in-

organic phosphates which are in various combinations with calcium, magnesium, iron, aluminum, manganese, and other ions. Such drastic treatment attacks the clay minerals and consequently releases phosphate ions which may be held on the surface of the colloids. Only the very resistant forms of phosphate remain undissolved.

(2) *Soil phosphorus soluble in dilute acids.* Dilute acids are somewhat more selective than the strong concentrated acids in the form of phosphates dissolved. Fraps (1906) was among the early workers to study the solubility of different phosphate minerals in dilute acids and reported that freshly precipitated phosphates of calcium, aluminum, and iron as well as apatite, vivianite, and triplite were dissolved in 0.2 *N* nitric or hydrochloric acids. Wavellite and dufrenite were only slowly soluble in acids at this concentration. Precipitated calcium phosphates were soluble in more dilute (0.005 *N*) acid. Stoddart (1909) reported similar results but showed further that wavellite and dufrenite were dissolved by sodium hydroxide. Fisher and Thomas (1935) studied the solubility of several phosphate minerals in solutions adjusted to different pH levels, and, although their results generally agreed with the earlier workers, it is obvious that clean separations are never actually realized.

Additional evidence that sharp separations of forms may not be realized by dilute-acid extractions is given by Peech (1945), who showed that, in a single extraction, each of the dilute-acid reagents have an equilibrium concentration representing the largest amount which can be removed from a given soil. The uptake of phosphorus from solution in the presence of a dilute-acid extracting reagent was also studied by Neller and Comar (1947), Cooke (1951), and Heck (1934b). The effect of the anion of the acid on the readsorption during extraction was studied by Russell and Prescott (1916) and by Demolon and Barbier (1930).

The anion of the acid as well as the concentration of hydrogen ion is important in determining the solubility of many phosphate compounds. Russell and Prescott (1916) and Demolon and Barbier (1930) found that citric and oxalic acids were particularly effective. This effect will be discussed further in a later section.

Dilute acids are widely used in diagnosing needs for phosphorus fertilizers, and research in this area is extensive and in itself subject of a review in this symposium. For completeness here, however, it should be said that the 0.2 *N* acid extraction was proposed for this purpose by Fraps (1906), Stoddart (1909), and Shedd (1921) because it would readily dissolve various combinations of calcium and phosphorus and attack more slowly the iron and aluminum phosphates. This approach

is in contrast to that of Dyer (1894) and Truog (1930), who aimed to adjust the acid strength to approximately that operating at the root surface in plant feeding. In both these latter cases the extracting solutions were such that a constant pH tended to be maintained during the extracting period. The anions in the two acids would, however, from present knowledge be expected to have a very different effect on the form of phosphate extracted.

Significantly, extractants used in determining the phosphorus status of soils dissolve at least partially the phosphate-calcium forms. The nature of these forms is discussed in Chapter IV but, they are also important in neutral and acid soils.

Agricultural soils may usually be considered calcium systems. Even in humid areas of acid soils, the calcium ion is preferably the dominant one in the cation exchange complex and liming practices have developed to assure this condition. The calcium-phosphate complexes are expected in increasing amounts as neutrality is approached. Burd (1948) placed great emphasis on calcium forms, considering them as playing a dominant role in phosphorus nutrition of plants in most soils even at pH levels well below neutrality. He did not regard the calcium forms as a "definite molecular species" (i.e., having a definite Ca:P ratio) having a definite solubility but as a mineral species of secondary origin. A limed soil can be expected to be extremely heterogeneous in respect to pH. Micro areas next to lime concentrations or clay particles of a high calcium saturation could be more alkaline and could contain appreciable amounts of the calcium complexes although the whole soil may well be quite acid. "Easily acid-soluble" phosphorus in soils might be expected to contain the calcium complexes with varying amounts of other forms.

c. Adsorbed Phosphorus and Phosphorus Soluble in Alkaline Solutions. In addition to workers mentioned above (Fraps, 1906; Stoddart, 1909), the solubility of iron and aluminum phosphates in alkaline solutions has been investigated by Stelly and Pierre (1942) and by Williams (1937), who also showed that the only phosphate forms definitely insoluble in sodium hydroxide are those of the apatite type.

Russell (1932) classified soil phosphorus compounds into three groups:

> "Inorganic phosphorus in neutral soils: probably a calcium phosphate: hydroxy apatite.
> Inorganic phosphorus in acid soils: presumably combinations with iron and aluminum oxides.
> Organic phosphates . . . "

In accord with the groupings by Russell, Dean (1938) proposed a fractionation procedure which called first for treatment of the soil with 0.25 *N* NaOH apparently aimed at extracting the iron and aluminum phosphates. The sample was extracted with 0.5 *N* H_2SO_4 to remove calcium forms. The portion not removed by these solutions was also determined by subtraction from the total.

Other analytical schemes for the fractionation of soil phosphorus have been proposed by Piper (1947), Bray and Kurtz (1945), Fraps and Fudge (1945), and Ghani and Aleem (1943a, 1943b). The procedures proposed by Piper and by Bray and Kurtz did not aim at accounting for all the soil phosphorus. Piper suggested that, in addition to acid extractions, an extraction with 0.1 *N* NaOH be used for determining "exchangeable" or adsorbed phosphate. Bray and Kurtz, following the work of Dickman and Bray (1941), used ammonium fluoride to remove adsorbed phosphates. In spite of differences in reagents and terminologies considerable parallelism exists between the different procedures. All would extract to greater or less degree the calcium complexes with an acid reagent; another form would be removed by solutions of hydroxide or fluoride; and a residual or inert fraction would remain unextracted. The degree of distinction which can be made between the iron and aluminum phosphates and the adsorbed phosphates is not entirely clear and will be discussed more fully in Section IV.

Amounts of phosphorus in the fractions of soils vary greatly. Dean (1938), in 34 soils from widely distributed sources, found that the acid-soluble fraction ranged from near zero to over 100 p.p.m. and made up to 40 per cent of total soil phosphorus. Amounts of alkali-soluble inorganic phosphorus were of the order of 50 p.p.m. to 600 p.p.m. with a maximum of 40 per cent of the phosphorus in this fraction. The mean percentages in the acid-soluble and alkali-soluble fractions were 10.9 and 18.9, respectively, with a tendency for the acid-soluble fraction to be larger in soils of higher pH and for the hydroxide-soluble to be higher in soils of low pH. In Hawaiian soils, Dean (1937) found variations from 40 to 135 p.p.m. in the acid-soluble fraction and from 170 to 390 p.p.m. in the alkali-soluble. The acid-soluble fraction in a group of untreated Illinois soils reported by Bray and Dickman (1941) ranged from near zero to over 300 p.p.m., while that soluble in 0.1 *N* NaOH ranged from 28 to 130 p.p.m.

In addition to data giving the amounts of acid-soluble phosphorus in surface soils, considerable data have been accumulated on the amounts of acid-soluble and other forms of phosphorus in soil profiles. Pearson *et al.* (1940) report total and acid-soluble (Truog method) phosphorus in horizons of twelve Iowa soils in which acid-soluble phosphorus was

as much as 78 p.p.m. in the surface and 250 p.p.m. in the subsoil. In general the lowest amounts of phosphorus were found in the lower A or upper B horizon. For other references on the amounts of phosphorus through soil profiles, the papers by Allaway and Rhodes (1951), Odynsky (1936), Wheeting (1924), and Stephenson and Chapman (1930) may be consulted as well as additional references cited by Pearson *et al.* (1940).

d. "Residual" or "Lattice" Phosphorus. A portion of the soil phosphorus, varying from a very small amount to over half the total phosphorus, is inert to extracting reagents mentioned in the above fractionation procedures. The nature of this residual portion is not known and has not been studied extensively.

Dean (1938) found this residual fraction to amount to 40 per cent of the total phosphorus on the average and that the proportion had remained practically unchanged during 50 years of cropping and fertilization in the Rothamsted and Woburn plots. Dickman and DeTurk (1938) accounted for nearly all the phosphorus by the summation of the organic and acid-soluble fractions in some young Illinois soils but found that a considerable portion could not be similarly accounted for in the older soils. Although these authors did not report an adsorbed fraction at that date, subsequent work (Bray and Dickman, 1941) indicated that the adsorbed phosphorus would not account for the remainder of the soil phosphorus.

The residual fraction is not likely to consist of titanium phosphates as is sometimes supposed. Fisher and Thomas (1935) found that titanium phosphate was soluble in the acid fraction. Dean (1937), in studying the phosphorus fractions in soil profiles of Hawaii, found that the surface soil contained two or three times as much titanium as the lower horizons but was much lower in residual phosphorus. Perkins and King (1943a) concluded that, while titanium minerals adsorbed phosphate, the amount could not be quantitatively important in most soils.

In a petrographic study, Fry (1913) identified occluded apatite in quartz particles from sand separates of several soils and found that this phosphorus was insoluble in acids. Plummer (1915), using Fry's methods, also found apatite present either as "prismatic" apatite or as "tiny needles enclosed in other minerals" in the sand fraction of several North Carolina soils. Since some of these soils were from mountain regions, a colluvial origin is suggested. Leahey (1935), making separations by heavy mineral techniques, was able to identify apatite in a Lexington soil and in a few other unusual soils.

Despite the evidence for the occurrence of apatite in certain soils it is nevertheless an unstable form in humid soils and is rarely found in

surface horizons (Jeffries, 1952, personal communication). The inert fraction can hardly be considered as the primary mineral. The amounts of inert phosphorus in many soils are too large to occur as occlusions in other minerals. Occlusion of appreciable amounts of apatite in the clay particles seems unlikely but large amounts of inert phosphorus were found by Robinson and Holmes (1924) in the clay separate from soils of many different locations. Marshall (1935) also found an inert fraction in all the clay from some Missouri soils and suggested that the phosphate ion could be present in the clay mineral lattice in positions normally occupied by the silicate ion. In the absence of new evidence to the contrary, the "lattice" form of inert phosphorus seems the most plausible.

III. Reactions of Added Phosphates in Soils

Research to discover the nature of the reactions of phosphate in soils has been spurred by economic considerations. Efficiency of fertilizer use has received great emphasis in periods of fertilizer scarcity or of economic stress and more complete recovery of phosphate fertilizer by plants has been the object of many studies of "phosphate fixation," which was presumed to prevent that recovery. A review of some types of reactions by which phosphate is removed from solution and is "fixed" in the soil is attempted in the following sections.

1. Precipitation by Ions in the Soil Solution

Among the explanations assigned to the removal of phosphate ions from their solutions when in contact with soils is the formation of sparingly soluble compounds with cations of the soil solution. Ions of calcium, magnesium, iron, aluminum, manganese, titanium, and others have been suggested at one time or another as precipitating agents. Gaarder (1930) studied the precipitation of phosphate by iron and aluminum at different pH levels. In an era when the science of chemistry was largely concerned with stoichiometric reactions, the formation of compounds of definite molecular ratios appeared logical and reasonable. Fisher (1922) had defended this viewpoint and criticized the alternate views advanced by the workers of the period. He cited the work of Hall and Amos (1906), who had concluded that their studies of the solubility of native phosphorus indicated "the presence in the soil of several compounds of varying solubility." When working with manured soils, however, Hall and Amos had found a logarithmic decrease in solubility, "indicating the presence of one particular phosphate dissolving in proportion to the mass of it present." Comber (1924) followed the reasoning of Fisher to deny the existence of the "alleged

amphoteric properties" of soils. Fisher's argument, covering both cations and anions, would appear unusual in the light of presently accepted concepts of clay mineral structures and cation exchange, in which calcium ions when taken up by the soil are not usually considered as precipitated in sparingly soluble calcium compounds.

In recent years several investigations have been aimed at establishing the conditions under which ions of the soil solution form precipitates of new, discrete particles of a phosphate mineral. Haseman *et al.* (1950a) treated goethite, gibbsite, illite, kaolinite, and montmorillonite with phosphate solutions and different bases and were able to isolate and identify, by optical and other methods, crystals of palmerite-like phosphate minerals with a formula $(H, K, Na, NH_4)_2(Al, Fe)(PO_4)_2 \cdot nH_2O$ in which iron and aluminum could be present in widely varying proportions. If the cations (H, K, Na, NH_4) were not present, an isomorphous series of variscite-barrandite-strengite, $AlPO_4 \cdot 2H_2O$-$(Al, Fe)PO_4 \cdot 2H_2O$-$FePO_4 \cdot 2H_2O$, was found and identified. In a later paper Haseman *et al.* (1950b) report further work in nonsoil systems showing that taranakite, $2(K,NH_4)_2O \cdot 3Al_2O_3 \cdot 5P_2O_5 \cdot 26H_2O$, and three other groups of similar minerals could be formed under conditions similar to those in soils. The formula of each of the minerals postulated permits extensive isomorphous substitution and would result in an almost unlimited array of solubilities, properties, and compositions.

Cole and Jackson (1950a) have also been able to identify, by X-ray diffraction, minerals of the variscite-barrandite-strengite isomorphous series which had been prepared *in vitro*, and they have studied (1950b) the solubility products in the variscite, $Al(OH)H_2PO_4$, system and in the minyulite, $K[Al(OH)_2H_2PO_4]_2OH$, system. In this work the minimum solubility at the equilibrium pH was 4.0 in the variscite system and around 6.5 in the minyulite system. The minyulite, however, was apparently unstable and with further time changed to variscite with the lower equilibrium pH.

According to Cole and Jackson (1950a), "Precipitation of the variscite series in soils takes place in the form of its crystals as a new, separate solid phase, and therefore its precipitation is distinct from adsorption. . . . True, these crystals may build up intimate association with the soil minerals serving as sources of aluminum and iron, possibly though not necessarily beginning as a single chemisorbed layer of phosphate ions." This view of precipitation as discrete crystals is similarly expressed by Haseman *et al.* (1950a): "It is suggested that under some conditions phosphate may become fixed in the soil as substituted palmerites and compounds of the variscite-barrandite-strengite isomorphous series. The escape of such crystalline products of the fixation re-

actions from detection in natural soils is attributed to the extremely small size of the crystals." However, Haseman *et al.* (1950b) discussed the possibility of the initial stage of the reaction as being a " . . . combination of phosphate ions with the superficial ions of aluminum and iron that are held at the extremities of the lattice or by exchangeable attachment on both the clays and the hydrous oxides of iron and aluminum." The later stage might, according to these authors, be a gradual decrease in " . . . solubility as a result of crystallization and partial dehydration to form phosphates similar to palmerite, variscite, or strengite."

Solubilities of phosphorus in these systems as reported by Cole and Jackson (1950a) and by Haseman *et al.* (1950b) are in good agreement —of the order of at least a few parts per million—and are considerably greater than those found naturally in soils. This solubility implies that added phosphate "fixed" in this form would maintain a considerably higher equilibrium value of phosphate in solution than do the native forms.

A possible explanation of the high solubility of these compounds in relation to soil phosphorus is the suggestion by Cole and Jackson (1950a) that the solubility is depressed by excess aluminum ions from gibbsite, kaolinite, or montmorillonite. Aging with a reorientation of the ions and dehydration of the phosphate precipitate might also be expected to decrease the solubility of these precipitates below that encountered in the laboratory experiments, where the maximum time involved was less than 60 days.

Among earlier investigations which led to a similar conclusion was that by Metzger (1940), who worked with prairie soils and concluded that "absorption or precipitation" accounted for fixation and not "surface phenomena."

An explanation that phosphate is held in the soil by simple precipitation sometimes leads to rather questionable conclusions. Precipitation frequently connotes the formation of a definite compound of constant composition and equivalent ratios. This idealized compound would furthermore have a definite solubility and maintain at equilibrium a certain concentration of phosphate in solution as long as the solid phase was present. If the phosphate in a given soil were present as a series of insoluble compounds, the idealized situation would call for a stepwise decrease in solubility in a series of extractions. The solubility should be nearly constant until all of the most soluble compound dissolved, when the concentration in solution would then assume a level characteristic of the compound of next-lower solubility.

The observed solubility of soil phosphate shows no such stepwise

changes but decreases very gradually with repeated extractions or dilutions. This gradual decrease is evidence, but not necessarily proof, that definite phosphate compounds are not present in soil. In isolated solutions phosphates of calcium, iron, aluminum, and other ions are difficult to precipitate in exactly the stoichiometric proportions of a definite compound, and once precipitated do not show a definite solubility. Holt *et al.* (1925) made extensive studies of calcium phosphate systems and found that the solubility product was difficult to establish and varied in the presence of soluble salts and other conditions. The same situation exists to a greater degree with phosphates of iron, aluminum, and manganese and the precipitation of single simple compounds of one of these ions in a diverse system like soil seems highly unrealistic.

The precipitation explanation often conveys the impression that the precipitating ions are present in the soil solution and will disappear from solution in definite proportions to the phosphate ions added. Such a direct relation is very difficult to show in complex soil systems. Generally, except for very acid soils, the concentrations of iron, aluminum, and manganese in the soil solution are very low and could account for only a small removal of phosphate (Magistad, 1925; Bear and Toth, 1942).

Another weakness in the precipitation explanation is that the possible compounds have minimum solubilities at pH levels not common in agricultural soils. The pH ranges for stability of the variscite-strengite systems have been mentioned.

2. *Reactions of Phosphates with Soil Particles*

a. Reactions with Hydrated Sesquioxides. Sesquioxides form in processes of weathering and are present to some degree in nearly all soils either as separate particles or as coatings on the other particles. These oxides form and exist in varying degrees of hydration and have been studied extensively as reactants with phosphates both in the presence of soils and in isolated systems.

The hydrated oxides of iron and aluminum react with phosphate and under some conditions result in the same products discussed under precipitation reactions in the previous section. In some cases, the phosphate ions have been considered as attaching merely to the surface of the hydrated oxides as in an adsorption reaction and in other cases the reaction proceeds further to form the definite phosphate compound. In many respects, a distinction between reactions in which phosphate ions are precipitated from solution by ions of iron and aluminum and reactions in which phosphate ions are removed from solution by hydrated oxides is arbitrary, since the final products, if both reactions went to completion, would be identical.

Warington (1866) was apparently the first to observe the reaction of phosphate ions with hydrated oxides of iron and aluminum. After further study (1868) he concluded that these reactions were chemical in nature and resulted in iron and aluminum phosphates, citing a contemporary paper by Peters (1867) which mentioned similar work.

Fraps (1911), who was among the early soils workers in this country to study the properties of iron and aluminum phosphates, found that the solubility of phosphate in dufrenite, wavellite, and variscite was increased tenfold by ignition. Later Ford (1933) found that natural hydrated oxides of iron and aluminum removed a high proportion of soluble phosphate from solution and that X-ray analysis of the resulting material indicated that a different crystalline compound was formed. The "fixed" phosphate was insoluble in 0.002 *N* sulfuric acid. The hydrated oxides, goethite and limonite, lost this ability to "fix" phosphate upon heating, and the natural nonhydrated oxides, hematite and bauxite, took up little phosphate.

Heck (1935) studied the solubility of native and applied phosphate in a variety of soils and related it to the solubilities of phosphate compounds, which Ford had indicated could be formed in reactions between phosphate ions and hydrated oxides. Both Heck and Ford considered "fixed" phosphate as that which could not be extracted with 0.002 *N* H_2SO_4 buffered to pH 3.0, and Heck (1934a) gave formulas of a number of minerals which might be formed with the hydrated oxides at the lower soil pH levels when soluble phosphates are added. Among these minerals were vivianite, strengite, dufrenite, variscite, and wavellite.

Reactions of phosphate ions with artificial gels of silica, alumina, and iron were studied by Gordon and Starkey (1922), Starkey and Gordon (1922), and Lichtenwalner *et al.* (1923), who found that phosphate was taken up in proportion to concentrations in the added solutions and was subsequently released slowly in a series of water extractions. Adsorption of phosphate ions increased as the pH was decreased, while the adsorption of nitrate and sulfate ions was much smaller and much less affected by pH levels. Silica gel adsorbed little phosphate (Wiley and Gordon, 1922).

Tiulin (1936) ascribed "fixation" of phosphate to sesquioxides and also studied the uptake and release of soluble phosphates by iron gels and obtained results similar to those of Starkey and co-workers. The reactions with gels were considered surface reactions; Tiulin discussed mechanisms of adsorption and favored an explanation in which both cations and anions were probably adsorbed in ionic layers around definite areas of the crystal lattice and believed that in these layers phosphate ions could be replaced by certain other anions. Starkey and Gordon (1922), regarded the reactions as adsorption reactions but felt

that there was little basis of choice for a particular mechanism. Russell and Prescott (1916) had studied the reactions of soils with different anions and the effect of time and concentration on the amounts taken up. These workers concluded that the phenomenon was one of "adsorption—the concentration of one substance on the surface of another" but proposed no exact mechanism. Prescott (1916) reviewed the work of previous investigators and the theories on the absorption by soils. Fisher (1922) severely criticized this concept and explained the uptake of oxalate by soils as a precipitation by calcium and of citrate by iron and aluminum. This criticism, based on the limited knowledge then available about the nature of soil colloids, probably tended to discourage investigations of anion adsorption.

b. Reactions with Clays. Developments in the concepts of clay mineral structures and cation exchange stimulated investigations of the reactions of phosphate ions with clay particles after precautions had been taken to remove all easily soluble metal ions and sesquioxides. Thus, Roszmann (1927), using dialyzed clay from a Putnam soil, observed a considerable uptake of phosphorus and drew some comparisons between that reaction and cation exchange. Scarseth and Tidmore (1934b) also found retention of phosphates by several clays which had been purified by electrodialysis and found that clays with a low silica:sesquioxide ratio held more phosphate against extractions with dilute acids. Toth (1937) also showed that the removal of iron oxides reduced phosphate retention.

(*1*) *Mechanisms of adsorption.* No single explanation is sufficient to cover all cases of phosphate uptake by clays, and a number of mechanisms for these reactions have been proposed. General practice is now to group those which occur at the colloid surface and result in a "concentration at the interface" as adsorption reactions. The term adsorption does not imply, as was formerly the case, that only "physical" and not "chemical forces" are involved. This current usage has been criticized (Kelley, 1946) but will be accepted throughout this discussion. The term adsorption, which admittedly covers a number of mechanisms, is justified by the fact that the phosphate held on the colloid is a function of the concentration in solution, and that solubility of this adsorbed phosphate is related to the amount adsorbed rather than to the solubility of any particular compound. A somewhat more logical classification and terminology for different types of phosphate fixation has been described diagrammatically by Williams (1949).

Following the work of Roszmann (1927), Bradfield *et al.* (1935) proposed three mechanisms for phosphate reaction with clays. These mechanisms were essentially those used by Scarseth (1935), who found

retention in the pH range of 5 to 6 by a sodium clay and suggested that the phosphate ion replaced a hydroxyl from an aluminum ion at the surface of the colloid. At slightly acid reactions a second mechanism evidenced by increased adsorption in clays containing exchangeable calcium was thought to be due to a linkage of the phosphate through calcium ions in exchange positions. Retention at low pH levels (pH 3.0 to 4.0) was explained by precipitation by ions of iron and aluminum which come into solution under those conditions. Phosphate retention under these three conditions was later supported by Allison (1943), who worked with clays which had been purified by a biological reduction method (1942).

(2) *Anion exchange.* A number of studies have been made to determine the nature and extent of anion exchange in soils and clays. The suggestions on anion exchange by Prescott (1916) and Russell and Prescott (1916) have been mentioned, and further discussion was given by Mattson (1931). Antoniani (1927) and Antoniani and Fonio (1929) attempted to use arsenate solutions to replace adsorbed phosphate and observed arsenate adsorption by the soil. Conrad (1939) demonstrated retention of phosphate compounds which do not form insoluble salts with the soil constituents. Burd and Murphy (1939) used sodium hydroxide to displace adsorbed phosphate and took into account this fraction and the anion-adsorption capacity along with the usual easily acid-soluble fraction for the prognosis of phosphate deficiency in soils. Dickman and Bray (1941) proposed the use of fluoride to displace adsorbed phosphate, and Piper (1947) suggested a method for determining the anion-exchange capacity.

In a series of detailed studies, Dean and Rubins (1947a, 1947b) and Rubins and Dean (1947) showed that phosphate and arsenate could be alternately adsorbed and then mutually replaced. Replacement of phosphate by other anions (fluoride, tartrate, and citrate) was also compared, but an equivalent anion-for-anion exchange was not found. These investigators considered that the adsorption being studied was an exchange for hydroxyls at the edges of the lattice and in support of this mechanism gave data showing a general relation between the anion-exchange capacity and the specific surface. Marshall (1949), in discussing anion exchange in clays, considered that the hydroxyl ions associated with aluminum ions at the crystal edge would be exchangeable, and if this were the case the ratio of cation:anion exchange capacities should be around 1:1 in kaolinitic clays. Mehlich (1948) has determined such ratios in a number of clays and soils and has found considerable variation among kaolinites. Some of this variation can be explained by impurities, but Mehlich (1950) found a ratio of somewhat

greater than 1:1 even after the kaolinite was treated to remove hydrous oxides. Different methods of determination, especially of the anion-exchange capacity, by different investigators can be expected to produce discrepancies in these ratios.

Murphy (1939) explained retention and low availability of phosphate retained by kaolinite and kaolinitic soils by an exchange of added phosphate with hydroxyl ions of the hydroxyl layers in the kaolinite crystal lattice. This explanation was supported by Stout (1939), who found that phosphating ground kaolinite changed the X-ray pattern and that the water formed from released hydroxyls was equivalent to the phosphate adsorbed. A similar interpretation of the reaction between kaolinite and phosphate was given by Black (1941). Kelly and Midgley (1943) demonstrated the release of hydroxyls from iron hydroxide and ground kaolinite during reactions with phosphate and pointed out that these reactions in the case of the iron hydroxide would result in a hydrated iron phosphate. With kaolinite an analogous reaction would result in "kaolinite phosphate." in which aluminum ions in the surface of the kaolinite retained the phosphate ion.

Sieling (1946), after extended study of the reactions of phosphate and arsenate ions with ground kaolinite, concluded that the chief reaction was not between phosphate and kaolinite but between a product of the grinding, "possibly a hydrous alumina such as —AlOOH," and that hydroxyls were released during the reaction. Ensminger (1948) also demonstrated a release upon heating of water equivalent to phosphate taken up by hydrated oxides and clay minerals. Low and Black (1947) found that kaolinite could be decomposed by concentrated phosphate solutions with the formation of some type of aluminum phosphate compound and a release of silica. Citrate extraction of the "fixed" phosphate removed aluminum in constant equivalent ratio to phosphorus and was taken as proof that an aluminum phosphate compound had been formed. This explanation that the anions effective in removing phosphate are those which combine with the precipitating cation is in agreement with the explanation given by Teakle (1928) for the effect of oxalate. Sieling and co-workers (Swenson *et al.*, 1949; Struthers and Sieling 1950; and Dalton *et al.*, 1952) have studied the effects of anions on dissolving or preventing precipitates of the phosphates of the sesquioxides. The ability of an anion to extract the phosphate ion from either an absorbed or a precipitated condition is apparently closely related to its ability to complex with iron and aluminum. The role of complex formation in this connection was probably first suggested by Davis (1935).

From the preceding paragraphs it is evident that no single mechanism is involved in the reaction of phosphate ions with soil particles

or even in the exchange with hydroxyls. The evidence indicates that phosphate ions may be taken up by the hydrated sesquioxides with an equivalent release of hydroxyls. If this reaction is limited in extent, affecting only surface hydroxyls, a surface reaction or "adsorption" would occur. Concentrated solutions and longer time periods would result in an extensive reaction and a "precipitation" of a hydrated phosphate of iron or aluminum. Evidence of two types of reactions between the clay particle and the phosphate in solution was found by McAuliffe *et al.* (1947) and by Low and Black (1950). The latter authors presented the hypothesis that in concentrated solutions phosphatolysis of kaolinite proceeded by an exchange of phosphate in solution for silicate ions in the outer layer of the lattice and that this exchange was followed by a decomposition of the lattice and precipitation of an aluminum phosphate compound. In dilute-solution fixation ". . . obeyed the Freundlich adsorption isotherm and increased with temperature. Since the amount of phosphate involved in this reaction was small compared with silica release, it was concluded that the dilute-solution adsorption represented a different reaction—perhaps the replacement of surface hydroxyl groups by phosphate groups."

Release of silica during phosphate adsorption has been observed by Mattson and Hester (1935), by Toth (1937), and, as mentioned in the previous paragraph, by Low and Black (1950). Growth responses from added silicates have been attributed to increased availability of phosphate due to replacement or reduction of fixation of phosphate by the silicate ions (Toth, 1939; Weiser, 1933; Schollenberger, 1922). Quantitative relationships involved in this exchange have, however, not been clarified.

Other mechanisms of adsorption are probably possible and have been suggested. Just as cation-exchange spots result on the crystal surface from substitution within the lattice of cations of smaller charge, e.g., Mg^{++} for Al^{+++}, a negative exchange position might arise from the reverse substitution. Such a type of "counter ion" adsorption, if it occurs, has not been separated from anion exchange occurring at the exposed iron and aluminum ions in the lattice edges. "Saloid" bound anions in an ion swarm around the particles have been suggested and would, if present, be confused in determination with exchangeable anions of other types.

Bloch (1950) has demonstrated chloride adsorption by surface precipitation with silver ions in the cation-exchange complex. A similar reaction should be presumed even more probable with phosphate and may be analogous to reactions with calcium ions in slightly acid soils. Another interesting mechanism for anion exchange has been suggested

by Mortland and Gieseking (1949), who studied anion adsorption by amino groups of polyamine compounds which had previously been adsorbed by clays. This type of anion adsorption is probably not important in the soil.

3. *Factors Influencing Phosphate Retention*

The course and extent of the reaction of added phosphates in soils may be influenced by a number of variables. Many of these have been touched upon in the preceding discussion and are enumerated below with little additional discussion.

a. Concentration of Phosphate Ions in Solution. Under many conditions the extent of adsorption is governed primarily by the concentration of added phosphate in solution. This concentration effect is particularly important in the initial short-time reaction before equilibrium is attained between the phosphate on the colloid and in the solution. Hibbard (1935) stated that soils had no definite "fixing power" but that fixation was a function of the concentration in the solution at equilibrium. Dean and Rubins (1947a) and Ravikovitch (1939) also showed the relation of concentration, and Russell and Prescott (1916), Davis (1935), Kurtz *et al.* (1946), and Low and Black (1950) demonstrated that the adsorption agreed with the Freundlich adsorption equation. Low and Black have shown that the type of reaction (see Section III.2.b.) can also be determined by concentration.

b. Time of Reaction. The reaction of phosphate with soils and clays can probably never be considered entirely complete as long as an appreciable concentration of phosphate remains in solution. Some of the surface reactions (adsorption in the ion atmosphere, counter ion adsorption, and possibly exchanges of some types of surface hydroxyls) are completed quickly and the rate of reaction decreases rapidly. Reorientation of adsorbed ions, dehydration of the products formed, and phosphatolysis of the clays may apparently continue almost indefinitely at a very slow rate.

c. Temperature. The rate of adsorption is increased by increased temperature, but the nature of the reaction is considered unchanged (Low and Black, 1950). Investigators (Heck, 1934b; Bass and Sieling, 1950) have utilized increased temperatures to speed the reaction when attempting to determine the "phosphate-fixing capacity" of soils.

d. Reaction (pH) of the Solution. The effect of pH upon phosphate retention by clays has been discussed. Maximum adsorption at low pH levels, 3.0 to 4.0, has been reported and is usually regarded as due to decomposition of the clay and precipitation of phosphates of the sesquioxides. Kaolinite and montmorillonite have been studied most fre-

quently, but Perkins (1948) found increased adsorption at the low pH level by a number of soil minerals.

In the absence of exchangeable calcium, adsorption decreases above neutrality because of the replacing effect of the hydroxyl ions. The increased adsorption at these lower pH levels is more pronounced with time for both kaolinite and montmorillonite. In periods of 24 hours or less pH has little effect on the uptake by montmorillonitic clays (Coleman, 1944a).

e. Type of Mineral. According to Murphy (1939) and Stout (1939), kaolinite has a large capacity to take up phosphate because of an exchange of phosphate with the layers of hydroxyl ions in the surface of the mineral. The large capacity of kaolinite has been reported by several investigators, Chatterjee and Datta (1951) being among the most recent. Perkins and King (1944) and Coleman (1942a) observed little difference between montmorillonite and kaolinite. Black (1943) and Coleman (1944a) found that kaolinite fixed more phosphate than did montmorillonite at low pH levels, but that little difference existed above pH 5.0. Marshall (1949), on the basis of crystal structure, predicted that hydrated halloysite would have a higher ability to adsorb anions than would kaolinite. Perkins (1943b) has studied phosphorus retention by a number of soil minerals.

f. Particle Size. Phosphate adsorption increases with decreasing particle size and finer clay fractions have appreciably greater anion-adsorption capacities than coarser fractions (Coleman, 1944b; and Perkins and King, 1944). This greater capacity would be expected in the finer fractions with their greater specific surface and larger number of active ions at the lattice edges.

g. Effect of Exchangeable Cations. Even at pH levels below neutrality, where calcium precipitation would not be expected, calcium clays retain more phosphate than do sodium, ammonium, or potassium clays (Gilligan, 1938; Heck, 1934c; Scarseth and Tidmore, 1934a; Chandler, 1941; Pratt and Thorne, 1948; Ravikovitch, 1934). Whether this additional retention is a precipitation of a calcium phosphate at the colloid surface or, as suggested by Scarseth (1935), a linking of phosphate to the colloid through a calcium ion on the exchange complex is not clear. This mechanism might explain the increased cation-exchange capacity observed to result from phosphate adsorption (Toth, 1937; Hester, 1937; Davis, 1945; Coleman and Mehlich, 1948).

h. Effect of Salts. Phosphate adsorption is influenced by the presence of electrolytes in the solution. In general this effect has been to increase adsorption (Kurtz *et al.*, 1946; Low and Black, 1950; Lehr and Van Wesemael, 1952), but recent studies by Wild (1950b) show that the

chlorides of potassium and sodium, while increasing adsorption in pH ranges of 6 to 7, have little effect below pH 3.6, and that potassium sulfate actually decreases adsorption at this low pH level. Wild attributes this salt effect to an influence on the solubility of slightly soluble phosphate compounds and cites (1950a) a number of papers on the effect of salt solutions on the solubility of phosphates of calcium, iron, and aluminum, as well as on soil phosphates. The effect of special anions in dissolving or replacing phosphate has been discussed. Conceivably, increased electrolyte would increase the concentration of an ion atmosphere about the colloid and phosphate would be loosely held in this atmosphere provided it is more strongly attracted to the colloid than to the anion of the added salt.

IV. Crop Utilization of Different Forms of Phosphorus

Many investigators have attempted to study in isolated systems the utilization by plants of the compounds alleged to form during phosphate fixation reactions. These studies have given variable results and cannot be interpreted with a high degree of precision.

1. Utilization of Iron and Aluminum Phosphates

As was mentioned previously, many combinations of phosphate with iron and aluminum are possible. The properties of these materials are probably dependent on the degree of crystallinity, age, and proportion of metal, hydroxyl, and phosphate ions.

Early trials by Patterson (1907) with iron and aluminum phosphates as fertilizers in field experiments gave excellent results. Trials in sand culture with precipitated iron and aluminum phosphates by Ellett and Hill (1910) gave yields as large and about 75 per cent as large, respectively, as superphosphate. Truog (1916), working with chemically pure materials, found that aluminum phosphate was extensively utilized by a variety of plants, giving yields from 75 to 100 per cent as great as superphosphate. Iron phosphates, especially ferrous phosphate, gave somewhat less crop growth. Marias (1922) summarized the work of several investigators in addition to those mentioned above; he studied further a number of natural iron and aluminum phosphates and found that their solubility could be increased greatly by heating to drive off the water of hydration. In pot cultures with soils to which iron phosphate was added, Scarseth and Tidmore (1934b) obtained yields of sorghum of around 24 per cent relative to superphosphate. Brown (1937), using the natural iron and aluminum phosphates, variscite and wavellite, similarly obtained beet yields about 75 per cent of that resulting from the addition of superphosphate. McGeorge and Breazeale

(1932) found that freshly precipitated iron and aluminum phosphates gave relatively high yields and were quite different from mineral phosphates. Dalton *et al.* (1952), in sand culture with corn plants, obtained yields relative to soluble phosphate of the order of only 15 per cent from freshly precipitated iron and aluminum phosphates. Some of the variation in the results reported on the utilization of iron and aluminum phosphates may be explained by the work of Fujiwara (1950a), who generalized that the extent of crystallization influenced the solubility of both natural and artificial phosphates of iron and aluminum, and that the solubility of the freshly prepared materials decreased upon aging, although precautions were taken to prevent dehydration (1950b).

2. Utilization of Phosphate Adsorbed by Gels of Iron and Aluminum Hydroxide

Wiley and Gordon (1923) and Tiulin (1936) found that phosphate adsorbed by gels of iron and aluminum hydroxide could be an excellent source of phosphorus and that the phosphorus which could be obtained by plants was proportional to the degree of saturation of the gel. Tiulin proposed a "critical saturation" below which this form of phosphorus would be insufficient for plant growth. This explanation was used by Williams and Stewart (1943) to explain phosphate fixation in certain Scottish soils.

3. Utilization of Phosphate Adsorbed by Soil and Clay Particles

Few experiments have been attempted in which adsorbed phosphorus was the sole source for plant growth. The available evidence, however, indicates that this form can be readily utilized. Dean and Rubins (1945) demonstrated uptake by barley plants of phosphate adsorbed on kaolinite. Coleman (1942b) obtained good growth of corn and oats from both montmorillonitic and kaolinitic clays which had previously been carefully purified and allowed to adsorb phosphate.

Supporting evidence that the adsorbed fraction can be readily utilized may be implied from the increase in this form in soils following additions of soluble phosphate fertilizers (Schollenberger, 1947; Dean and Rubins, 1947b).

V. Importance of Phosphate Fixation in Soil Fertility

Contrary to the apparent belief of two decades ago, more recent evidence indicates that the reactions of phosphate with soils are not entirely irreversible and that for most soils the term "fixation" is an exaggeration.

The belief that added phosphates were quickly converted to forms

which could be utilized by plants was based on incomplete recovery of fertilizer phosphate by plants, lack of response to phosphate fertilizer on certain soils, and a lack of solubility of added phosphate in extractants which measure the "available" phosphorus.

Evidence has accumulated that phosphate from newly added fertilizer furnishes only a fraction of the crop uptake and the portion not recovered by the first crop has definite residual value (Volk, 1945), although annual additions of some soluble phosphate may be necessary for maximum yields of certain crops. Low recovery of added phosphate, formerly attributed to phosphate fixation, is frequently due to other causes. Scarseth and Chandler (1938) and Ensminger and Cope (1947) made total analyses of soils which had received large additions of phosphate and found that much of the phosphate presumed to have been fixed was not actually present in the soil and had probably been removed by erosion.

Added phosphate cannot be assumed to be valueless to plants because it is not easily extracted by chemical reagents. Phosphate obtained in most of the rapid extraction procedures represents an equilibrium value and not a complete measure of the form. Coleman (1942b) obtained good crop growth on montmorillonitic and kaolinitic clays after different samples of each had been extracted respectively with water, dilute nitric acid, dilute sodium hydroxide, and dilute sulfuric acid buffered to pH 3.0. Coleman concluded that failure of crops to respond to added phosphate, often attributed to rapid fixation by the soil, was due to a sufficiency of phosphorus already in the soil and that large amounts of phosphorus formerly "considered fixed are available to plants." Williams (1951) also obtained good plant growth with acetic acid-extracted soils as the sole source of phosphorus.

In summary, the current viewpoint is that, in acid and neutral soils, phosphates react quickly to an adsorbed form which can be readily utilized by most crops. In time this initial form is gradually converted to a less soluble form which is less available. The duration of this conversion depends on the concentrations involved and the phosphorus status of the soil, but it is usually of the order of several months. Recent discussions of the general problem of phosphate fixation have been given by Williams (1950) and Barbier *et al.* (1948).

References

Agriculture Committee on National Policy. 1945. Fertilizers in the post-war national economy. *Planning pamphlet* **42**. National Planning Association. Washington, D. C.

Allaway, W. H., and Rhodes, H. F. 1951. Forms and distribution of phosphorus in the horizons of some Nebraska soils. *Soil Sci.* **72**: 119–128.

ALLISON, L. E. 1943. The trend of phosphate adsorption by inorganic colloids from certain Indiana soils. *Soil Sci.* **55**: 333–342.

ALLISON, L. E., and SCARSETH, G. D. 1942. A biological method for removing free iron oxides from soils and colloidal clays. *J. Am. Soc. Agron.* **34**: 616–623.

ANTONIANI, C. 1927. The behavior of arsenic acid relative to the absorbent power of the soil. *Atti accad. nazl. Lincei* (6) **6**: 107–112 [C. A. **22**: 295 (1928); original not consulted].

ANTONIANI, C., and FONIO, G. 1929. The interchange between phosphoric acid and arsenic acid in soils. *Atti accad. nazl. Lincei* (6) **9**: 344–350 [C. A. **23**: 4006 (1929); original not consulted].

BARBIER, G., CHABANNES, J., and MARQUIS, A. 1948. Utilisation des engrais phosphates par les plantes, après leur absorption dans le sol. *Plant and Soil* **1**: 11–17.

BASS, G. B., and SIELING, D. H. 1950. Method for determining the relative phosphate fixing capacity of acid soils. *Soil Sci.* **69**: 269–280.

BEAR, F. E., and TOTH, S. J. 1942. Phosphate fixation and its practical control. *Ind. Eng. Chem.* **34**: 49–52.

BLACK, C. A. 1941. The penetration of phosphate into the kaolinite crystal. *Soil Sci. Soc. Amer. Proc.* **6**: 157–161.

BLACK, C. A. 1943. Phosphate fixation by kaolinite and other clays as affected by pH, phosphate concentration, and time of contact. *Soil Sci. Soc. Amer. Proc.* **7**: 123–133.

BLOCH, J. M. 1950. Fixation des halogenures d'argent sur la montmorillionite. *Trans. 4th Interm. Congr. Soil Sci.* **3**: 32–33.

BRADFIELD, R., SCARSETH, G., and STEELE, J. G. 1935. Factors affecting the retention of phosphate by clay. *Trans. 3rd Intern. Congr. Soil Sci.* **1**: 74–75.

BRAY, R. H., and DICKMAN, S. R. 1941. Adsorbed phosphates in soils and their relation to crop response. *Soil Sci. Soc Amer. Proc.* **6**: 312–320.

BRAY, R. H., and KURTZ, L. T. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* **59**: 39–45.

BROWN, R. J. 1937. An improved sodium acetate buffer method for the determination of plant available phosphate and its application to irrigated Rocky Mountain soils. *Soil Sci. Soc. Amer. Proc.* **2**: 185–195.

BRYAN, O. C. 1933. The accumulation and availability of phosphorus in old citrus grove soils. *Soil Sci.* **36**: 245–259.

BURD, J. S. 1948. Chemistry of the phosphate ion in soil systems. *Soil Sci.* **65**: 227–247.

BURD, J. S., and MARTIN, J. C. 1923. Water displacement of soils and the soil solution. *J. Agr. Sci.* **13**: 265–295.

BURD, J. S., and MURPHY, H. F. 1939. The use of chemical data in the prognosis of phosphate deficiency in soils. *Hilgardia* **12**: 323–339.

CHANDLER, W. V. 1941. Phosphate adsorption by five Alabama soils as influenced by reaction, base saturation, and free sesquioxides. *J. Am. Soc. Agron.* **33**: 1–12.

CHATTERJEE, B., and DATTA S. 1951. Phosphate fixation by clay mineral montmorillonite and kaolinite. *J. Soil Soc.* **2**: 224–233.

CLARKE, F. W. 1920. Data of geochemistry. *U.S. Geol. Survey Bull.* **695**.

COLE, C. V., and JACKSON, M. L. 1950a. Colloidal dihydroxy, dihydrogen, phosphates of aluminum and iron with crystalline character established by electron and x-ray diffraction. *J. Phys. & Colloid Chem.* **54**: 128–142.

COLE, C. V., and JACKSON, M. L. 1950b. Solubility equilibrium constant of dihy-

droxy aluminum dihydrogen phosphate relating to a mechanism of phosphate fixation in soils. *Soil Sci. Soc. Amer. Proc.* **15**: 84–89.

COLEMAN, R. 1942a. The adsorption of phosphate by kaolinitic and montmorillonitic clays. *Soil Sci. Soc. Amer. Proc.* **7**: 134–138.

COLEMAN, R. 1942b. Utilization of adsorbed phosphate by cotton and oats. *Soil Sci.* **54**: 237–246.

COLEMAN, R. 1944a. The mechanism of phosphate fixation by montmorillonitic and kaolinitic clays. *Soil Sci. Soc. Amer. Proc.* **9**: 72–78.

COLEMAN, R. 1944b. Phosphorus fixation by the coarse and fine clay fractions of kaolinitic and montmorillonitic clays. *Soil Sci.* **58**: 71–77.

COLEMAN, N. T., and MEHLICH, A. 1948. Some chemical properties of soils as related to their cation-anion exchange ratios. *Soil Sci. Soc. Amer. Proc.* **13**: 175–178.

COMBER, N. M. 1924. The role of electronegative ions in the reactions between soils and electrolytes. *Trans. Faraday Soc.* **20**: 567–572.

CONRAD, J. P. 1939. Retention of phosphorus compounds by soils as shown by subsequent plant growth. *J. Agr. Research* **59**: 507–518.

COOKE, G. W. 1951. Fixation of phosphate during the acid extraction of soils. *J. Soil Sci.* **2**: 254–262.

DALTON, J. D., RUSSELL, G. C., and SIELING, D. H. 1952. Effect of organic matter on phosphate availability. *Soil Sci.* **73**: 173–181.

DAUBNEY, G. 1845. Memoir on the rotation of crops and the quantity of organic matters abstracted from soil by various plants under different circumstances. *Trans. Roy. Soc. (London) Phil.* 179–252.

DAVIS, F. L. 1945. Retention of phosphate by soils: II. Effect of drying and of certain cations on cation exchange capacity of soils. *Soil Sci.* **59**: 175–190.

DAVIS, L. E. 1935. Sorption of phosphates by non-calcareous Hawaiian soils. *Soil Sci.* **40**: 129–158.

DEAN, L. A. 1937. Distribution of the forms of soil phosphorus. *Soil Sci. Soc. Amer. Proc.* **20**: 223–228.

DEAN, L. A. 1938. An attempted fractionation of the soil phosphorus. *J. Agr. Sci.* **28**: 234–246.

DEAN, L. A. 1949. Fixation of soil phosphorus. *Advances in Agron.* **1**: 391–411.

DEAN, L. A., and RUBINS, E. J. 1945. Absorption by plants of phosphorus from a clay-water system: methods and ensuing observations. *Soil Sci.* **59**: 437–448.

DEAN, L. A., and RUBINS, E. J. 1947a. Anion exchange in soils: I. Exchangeable phosphorus and anion exchange capacity. *Soil Sci.* **63**: 377–406.

DEAN, L. A., and RUBINS, E. J. 1947b. Anion exchange in soils: III. Applicability to problems of soil fertility. *Soil Sci.* **63**: 399–406.

DEMOLON, A., and BARBIER, G. 1930. La concentration critique d'équilibre et l'appréciation du besoin des sols en acide phosphorique. *Proc. 2nd Intern. Congr. Soil Sci. Comm.* IV, pp. 86–96.

DICKMAN, S. R., and BRAY, R. H. 1941. Replacement of adsorbed phosphate from kaolinite by fluoride. *Soil Sci.* **52**: 263–273.

DICKMAN, S. R., and DETURK, E. E. 1938. A method for the determination of the organic phosphorus of soils. *Soil Sci.* **45**: 29–38.

DYER, B. 1894. On the analytical determination of the probably available plant food in soils. *Trans. J. Chem. Soc. (London)* **65**: 115–167.

DYER, B. 1902. Results of investigations on Rothamsted soils. *U. S. Dept. Agr. Off. Expt. Sta. Bull.* **106**: 98–112.

ELLETT, W. B., and HILL, H. H. 1910. Contribution to the study of phosphoric acid in soils and fertilizers. *Virginia Agr. Expt. Sta. Ann. Rept.*

ENSMINGER, L. E. 1948. The relation between water lost and PO_4 adsorbed on phosphating clay minerals and soil colloids. *Soil Sci. Soc. Amer. Proc.* **13**: 170–174.

ENSMINGER, L. E., and COPE, J. T., JR. 1947. Effect of soil reaction on the efficiency of various phosphates for cotton and loss of phosphorus by erosion. *J. Am. Soc. Agron.* **39**: 1–11.

FISHER, F. A. 1922. The phenomena of absorption in soils: a critical discussion of hypotheses put forward. *Trans. Faraday Soc.* **17**: 305–316.

FISHER, R., and THOMAS, R. P. 1935. The determination of forms of inorganic phosphorus in soils. *J. Am. Soc. Agron.* **27**: 863–873.

FORD, M. C. 1933. The nature of phosphate fixation in soils. *J. Am. Soc. Agron.* **25**: 134–144.

FRAPS, G. S. 1906. Availability of phosphoric acid of the soil. *J. Am. Chem. Soc.* **28**: 823–834.

FRAPS, G. S. 1911. Effects of ignition on solubility of soil phosphates. *J. Ind. Eng. Chem.* **3**: 335.

FRAPS, G. S., and FUDGE, J. F. 1945. The nature of phosphates dissolved by various soil extractants. *J. Am. Soc. Agron.* **37**: 532–541.

FRY, WM. H. 1913. The condition of the soil phosphoric acid insoluble in hydrochloric acid. *J. Ind. Eng. Chem.* **5**: 665–666.

FUJIWARA, A. 1950a. Effects of heating and dehydration on the constitution and availability of scarcely soluble phosphates. *Tôhoku J. Agr. Research* **1**: 223–228.

FUJIWARA, A. 1950b. Aging of scarcely soluble phosphate during long periods and its influence on availability. *Tôhoku J. Agr. Research* **1**: 229–232.

GAARDER, T. 1930. Die Bindung der Phosphorsäure im Erdboden. *Vestlandets Forst. Forsokstation, Meddelelse* **14**. Bergen.

GHANI, M. O., and ALEEM, S. A. 1943a. Fractionation of soil phosphorus: I. The distribution of some different forms of phosphorus in some Indian soils. *Indian J. Agr. Sci.* **13**: 283.

GHANI, M. O., and ALEEM, S. A. 1943b. Fractionation of soil phosphorus: II. Chemical nature of the phosphorus fractions. *Indian J. Agr. Sci.* **13**: 142–156.

GILLIGAN, G. M. 1938. Effect of degree of base saturation of soils upon the fixation of phosphate and potassium and the availability of phosphorus. *Delaware Agr. Expt. Sta. Bul.* **215**.

GORDON, N. E., and STARKEY, E. B. 1922. Influence of soil colloids on availability of salts. *Soil Sci.* **14**: 1–7.

HALL, A. D., and AMOS, A. 1906. The determination of available plant food in soil by the use of weak acid solvents: II. *Trans. J. Chem. Soc. (London)* **89**: 205–222.

HASEMAN, J. F., and BROWN, E. H., and WHITT, C. D. 1950a. Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* **70**: 257–271.

HASEMAN, J. F., LEHR, J. R., and SMITH. J. P. 1950b. Mineralogical character of some iron and aluminum phosphates containing potassium and ammonium. *Soil Sci. Soc. Amer. Proc.* **15**: 76–84.

HECK, A. F. 1934a. Phosphate fixation and penetration in soils. *Soil Sci.* **37**: 343–355.

HECK, A. F. 1934b. A method for determining the capacity of a soil to fix phosphorus in a difficultly available form. *Soil Sci.* **37**: 477–482.

HECK, A. F. 1934c. Effect of the degree of base saturation of a soil on its capacity to fix phosphorus in difficultly available form. *Soil Sci.* **38**: 463–470.

HECK, A. F. 1935. Availability and fixation of phosphorus in difficultly available form. *J. Am. Soc. Agron.* **27**: 874–884.

HESTER, J. B. 1937. Influence of phosphate fertilization on the amphoteric properties of coastal plain soils. *J. Am. Soc. Agron.* **29**: 10–16.

HIBBARD, P. L. 1935. Factors influencing phosphate fixation in soils. *Soil Sci.* **39**: 337–358.

HOLT, L. E., JR., LA MER, V. K., and CROWN, H. B. 1925. Studies of calcification: I. The solubility product of secondary and tertiary calcium phosphate under various conditions. *J. Biol. Chem.* **64**: 509–565.

HOPKINS, CYRIL G. 1910. Soil Fertility and Permanent Agriculture. Ginn and Company, Boston.

KELLEY, W. P. 1946. Modern concepts of soil science. *Soil Sci.* **62**: 469–476.

KELLY, J. B., and MIDGLEY, A. R. 1943. Phosphate fixation — an exchange of phosphate and hydroxyl ions. *Soil Sci.* **55**: 167–176.

KING, F. H. 1914. Soil Management. Orange Judd Co., New York.

KURTZ, T., DETURK, E. E., and BRAY, R. H. 1946. Phosphate adsorption by Illinois soils. *Soil Sci.* **61**: 111–124.

LEAHEY, ALFRED. 1935. Mineralogical and chemical studies on some of the inorganic phosphorus compounds in the soil. *Sci. Agr.* **15**: 704–712.

LEHR, J. J., and VAN WESEMAEL, J. C. 1952. The influence of neutral salts on solubility of soil phosphates. *J. Soil Sci.* **3**: 125–135.

LICHTENWALNER, D. C., FLENNER, A. L., and GORDON, N. E. 1923. Adsorption and replacement of plant food in colloidal oxides of iron and aluminum. *Soil Sci.* **15**: 157–165.

LIEBIG, J. VON. 1840. Chemistry and Its Applications to Agriculture and Physiology. Taylor and Walton, London.

LIEBIG, J. VON. 1863. The Natural Laws of Husbandry. John Blyth, Editor. D. Appleton and Co., New York.

LOW, P. F., and BLACK, C. A. 1947. Phosphate induced decomposition of kaolinite. *Soil Sci. Soc. Amer. Proc.* **12**: 180–184.

LOW, P. F., and BLACK, C. A. 1950. Reactions of phosphate with kaolinite. *Soil Sci.* **70**: 273–290.

MCAULIFFE, C. D., HALL, N. S., DEAN, L. A., and HENDRICKS, S. B. 1947. Exchange reactions between phosphates and soils: hydroxylic surfaces of soil minerals. *Soil Sci. Soc. Amer. Proc.* **12**: 119–122.

MCGEORGE, W. T., and BREAZEALE, J. F. 1932. Studies on iron, aluminum and organic phosphates and phosphate fixation in calcareous soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **40**.

MCLEAN, W. 1936. The determination of phosphorus in soils. *J. Agr. Sci.* **26**: 331–336.

MAGISTAD, O. C. 1925. The aluminum content of the soil solution and its relation to soil reaction and plant growth. *Soil Sci.* **20**: 181–226.

MARIAS, J. S. 1922. The comparative agricultural value of insoluble mineral phosphates of aluminum, iron, and calcium. *Soil Sci.* **13**: 355–410.

MARSHALL, C. E. 1935. The importance of the lattice structure of the clays for the study of soils. *Trans. J. Soc. Chem. Ind. (London)* **54**: 393–398.

MARSHALL, C. E. 1949. The Colloid Chemistry of the Silicate Minerals. Agronomy Monograph Vol. 1. Academic Press, New York.

MATTSON, S. 1931. Laws of soil colloidal behavior: V. Ion adsorption and exchange. *Soil Sci.* **31**: 311–331.

MATTSON, S., and HESTER, J. B. 1935. The laws of soil colloidal behavior: XV. *Soil Sci.* **39**: 75–84.

MEHLICH, A. 1948. Determination of cation- and anion-exchange properties of soils. *Soil Sci.* **66**: 429–445.

MEHLICH, A. 1950. Cation exchange-anion exchange ratios of kaolinitic soil colloids. *Trans. 4th Intern. Congr. Soil Sci.* **1**: 133–135.

METZGER, W. H. 1940. Significance of adsorption or surface fixation by some soils of the prairie group. *J. Am. Soc. Agron.* **32**: 513–525.

MIDGLEY, A. R. 1940. Phosphate fixation in soils—a critical review. *Soil Sci. Soc. Amer. Proc.* **5**: 24–30.

MOOERS, C. A. 1906. The soils of Tennessee, their chemical composition and fertilizer requirements. *Tennessee Agr. Expt. Sta. Bull.* **78**.

MORTLAND, M. M., and GIESEKING, J. E. 1949. Anion sorption and exchange by amine-clay complexes. *Soil Sci.* **68**: 391–398.

MURPHY, H. F. 1939. The role of kaolinite in phosphate fixation. *Hilgardia* **12**: 343–382.

NATIONAL PHOSPHORUS RESEARCH WORK GROUP. 1950. Summary of phosphorus research in the United States relating to soils and fertilizers. National Soil and Fertilizer Research Committee, F. W. Parker, Secretary. Soils Division, U. S. Department of Agriculture Bureau of Plant Industry, Soils, and Agricultural Engineering. Beltsville, Maryland.

NELLER, J. R., and COMAR, C. L. 1947. Factors affecting fixation of phosphorus in soils as determined with radioactive phosphorus. *Soil Sci.* **64**: 379–387.

ODYNSKY, W. 1936. Solubility and distribution of phosphorus in Alberta soils. *Soil Sci.* **16**: 652–664.

PARKER, F. W. 1927. Soil phosphorus studies: III. Plant growth and the absorption of phosphorus from culture solutions of different phosphate concentrations. *Soil Sci.* **24**: 129–146.

PARKER, F. W., and TIDMORE, J. W. 1926. The influence of lime and phosphatic fertilizers on the phosphorus content of the soil solution and of soil extracts. *Soil Sci.* **21**: 425–442.

PATTERSON, H. J. 1907. Fertilizer experiments with different sources of phosphoric acid. *Maryland Agr. Expt. Sta. Bull.* **114**.

PEARSON, R. W., SPRY, R., and PIERRE, W. H. 1940. The vertical distribution of total and dilute acid-soluble phosphorus in twelve Iowa soils. *J. Am. Soc. Agron.* **32**: 683–696.

PEECH, M. 1945. Nutrient status of soils in commercial potato-producing areas of the Atlantic and Gulf coast: Part II. Chemical data on the soils. *Soil Sci. Soc. Amer. Proc.* **10**: 245–251.

PERKINS, A. T. 1948. Phosphate fixation by soil minerals. *Soil Sci. Soc. Amer. Proc.* **13**: 99–101.

PERKINS, A. T., and KING, H. H. 1943a. Phosphate fixation by soil minerals: II. Fixation by iron, silicon, and titanium oxides. *Soil Sci.* **58**: 243–250.

PERKINS, A. T., and KING, H. H. 1943b. Phosphate fixation by soil minerals: mica and related groups. *Soil Sci. Soc. Amer. Proc.* **8**: 154–158.

PERKINS, A. T., and KING, H. H. 1944. Phosphorus fixation by soil minerals: III. Particle size. *Soil Sci. Soc. Amer. Proc.* **9**: 61–65.

PETER, A. M., and AVERITT, S. D. 1906. Soils. *Kentucky Agr. Expt. Sta. Bull.* **126**.

PETERS. 1867. Über das Verhalten der Phosphorsäure im Erdboden. *Ann. Landw.* p. 31 (cited by Warington; original not consulted).

PIERRE, W. H. 1948. The phosphorus cycle and soil fertility. *J. Am. Soc. Agron.* **40**: 1–14.

PIERRE, W. H., and PARKER, F. W. 1927. Soil phosphorus studies: II. The concentration of phosphorus in the soil solution and the availability of organic phosphorus to plants. *Soil Sci.* **24**: 119–128.

PIPER, C. S. 1947. Soil and Plant Analysis, pp. 137–153, 190–193. Interscience Publishers, New York.

PLUMMER, J. K. 1915. Petrography of some North Carolina soils and its relation to fertilizer requirements. *J. Agr. Research* **5**: 569.

PRATT, P. F., and THORNE, D. W. 1948. Solubility and physiological availability of phosphate in sodium and calcium systems. *Soil Sci. Soc. Amer. Proc.* **13**: 213–217.

PRESCOTT, J. A. 1916. Phenomenon of absorption in its relation to soils. *J. Agr. Sci.* **8**: 111–130.

RAVIKOVITCH, S. 1934. Anion exchange: I. Anion adsorption of phosphoric acid by soils. *Soil Sci.* **38**: 219–239.

RAVIKOVITCH, S. 1939. Influence of exchangeable cations on the availability of phosphate in soils. *Soil Sci.* **47**: 357–366.

ROBINSON, W. O., and HOLMES, R. S. 1924. The chemical composition of soil colloids. *U. S. Dept. Agr. Bull.* **1311**.

ROBINSON, W. O., STEINKOENIG, L. A., and FRY, WM. H. 1917. Variations in the chemical composition of soils. *U. S. Dept. Agr. Bull.* **551**.

ROSZMANN, C. A. 1927. Retention of phosphorus by soil colloids. *Soil Sci.* **24**: 465–474.

RUBINS, E. J., and DEAN, L. A. 1947. Anion exchange in soils: II. Methods of study. *Soil Sci.* **63**: 389–397.

RUSSELL, E. J. 1932. Soil Conditions and Plant Growth. Longmans, Green and Co., London.

RUSSELL, E. J., and PRESCOTT, J. A. 1916. The reaction between dilute acids and the phosphorus compounds of the soil. *J. Agr. Sci.* **8**: 65–110.

SCARSETH, G. D. 1935. The mechanism of phosphate retention by natural alumino-silicate colloids. *J. Am. Soc. Agron.* **27**: 596–616.

SCARSETH, G. D., and CHANDLER, W. V. 1938. Losses of phosphate from a light textured soil in Alabama and its relation to some aspects of soil conservation. *J. Am. Soc. Agron.* **30**: 361–374.

SCARSETH, G. D., and TIDMORE, J. W. 1934a. The fixation of phosphates by soil colloids. *J. Am. Soc. Agron.* **26**: 138–151.

SCARSETH, G. D., and TIDMORE, J. W. 1934b. The fixation of phosphates by clays. *J. Am. Soc. Agron.* **26**: 152–162.

SCHOLLENBERGER, C. J. 1922. Silica and silicates in relation to plant growth and composition. *Soil Sci.* **14**: 347–362.

SCHOLLENBERGER, C. J. 1947. Arsenate-displaceable phosphate in long fertilized and unfertilized plot soils. *Soil Sci.* **64**: 371–378.

SCHREINER, O., and FAILYER, G. H. 1906. The absorption of phosphates and potassium by soils. *U. S. Dept. Agr. Bur. Soils Bull.* **32**.

SHEDD, O. M. 1921. A short test for easily soluble phosphate in soils. *Soil Sci.* **11**: 111–122.

SIELING, D. H. 1946. Role of kaolin in anion adsorption and exchange. *Soil Sci. Soc. Amer. Proc.* **11**: 161–170.

STARKEY, E. B., and GORDON, N. E. 1922. Influence of hydrogen-ion concentration on the adsorption of plant food by soil colloids. *Soil Sci.* **14**: 449–457.

STELLY, M., and PIERRE, W. H. 1942. Forms of inorganic phosphorus in the C horizons of some Iowa soils. *Soil Sci. Soc. Amer. Proc.* **7**: 139–147.

STEPHENSON, R. E., and CHAPMAN, H. D. 1931. Phosphate penetration in field soils *J. Am. Soc. Agron.* **23**: 759–770.

STODDART, C. W. 1909. Soil acidity and its relation to the lack of available phosphates. *J. Ind. Eng. Chem.* **1**: 69–74.

STOUT, P. R. 1939. Alterations in the crystal structure of clay minerals as a result of phosphate fixation. *Soil Sci. Soc. Amer. Proc.* **4**: 177–182.

STRUTHERS, P. H., and SIELING, D. H. 1950. Effect of organic anions on phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* **69**: 205–214.

SWENSON, R. M., COLE, C. W., and SIELING, D. H. 1949. Fixation of phosphate by iron and aluminum and replacement by organic and inorganic ions. *Soil Sci.* **67**: 3–22.

TEAKLE, L. J. H. 1928. Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* **25**: 143–162.

TIULIN, A. Th. 1936. Availability of soil phosphates for the plant from the viewpoint of colloidal chemistry. *Soil Sci.* **42**: 291–299.

TOTH, S. J. 1937. Anion adsorption by soil colloids in relation to changes in free iron oxides. *Soil Sci.* **44**: 299–314.

TOTH, S. J. 1939. The stimulating effects of silicates on plant yields in relation to anion displacement. *Soil Sci.* **47**: 123–141.

TRUOG, E. 1916. The utilization of phosphates by agricultural crops, including a new theory regarding the feeding power of plants. *Wisconsin Agr. Expt. Sta. Research Bull.* **41**.

TRUOG, E. 1930. The determination of the readily available phosphorus of soils. *J. Am. Soc. Agron.* **22**: 874–882.

VAN BEMMELEN, J. M. 1888. Die Absorptionsverbindungen und das Absorptionsvermögen der Ackererde. *Landw. Vers. Stat.* **35** [quoted at length by Schreiner and Failyer (1906); original not consulted].

VOLK, G. W. 1945. Response to residual phosphorus of cotton in continuous culture. *J. Am. Soc. Agron.* **37**: 330–340.

WARINGTON, R. 1866. Researches on the phosphates of calcium and upon solubility of tricalcic phosphate. *J. Chem. Soc. (London)* **19**: 296–317.

WARINGTON, R. 1868. On the part taken by oxide of iron and alumina in the adsorptive action of soils. *J. Chem. Soc. (London)* **21**: 1–19.

WAY, J. T. 1850. On the power of soils to absorb manure. *J. Roy. Agr. Soc. Eng.* **11**: 313–379.

WEISER, V. L. 1933. Fixation and penetration of phosphate in Vermont soils. *Vermont Agr. Expt. Sta. Bull.* **356**.

WHEETING, L. C. 1924. Some physical and chemical properties of several soil profiles. *Michigan Agr. Expt. Sta. Tech. Bull.* **62**.

WILD, A. 1950a. The retention of phosphate by soil. *J. Soil Sci.* **1**: 221–238.

WILD, A. 1950b. The effect of neutral salts on the retention of phosphate by clay at various pH values. *Trans. 4th Intern. Congr. Soil Sci.* **1**: 146–149.

WILEY, R. C., and GORDON, N. E. 1922. Adsorption of plant food by colloidal silica. *Soil Sci.* **14**: 441–448.

WILEY, R. C., and GORDON, N. E. 1923. Availability of adsorbed phosphates. *Soil Sci.* **15**: 371–373.

WILLIAMS, E. G. 1949. Phosphate fixation. *N. A. A. S. Quarterly Rev.* **1**: 147–159.

WILLIAMS, E. G. 1950. Phosphate fixation and availability. *J. Sci. Food and Agr.* **1**: 244–248.

WILLIAMS, E. G. 1951. Effect of acid treatment of soils on phosphate availability and solubility. *J. Soil Sci.* **2**: 110–117.

WILLIAMS, E. G., and STEWART, A. B. 1943. Studies of phosphate fixation in Scottish soils: I. The recovery of added phosphate from a soil of the acid igneous group. *J. Agr. Sci.* **33**: 179–189.

WILLIAMS, R. 1937. The solubility of soil phosphorus and other phosphorus compounds in sodium hydroxide solutions. *J. Agr. Sci.* **27**: 258–270.

CHAPTER IV

Inorganic Phosphorus in Alkaline and Calcareous Soils

STERLING R. OLSEN

I. Introduction

The important phosphate chemistry in alkaline calcareous soils involves largely the nature and reactions of slightly soluble calcium phosphates naturally present in the soil and of the calcium phosphates resulting from the reactions between the soil and applied phosphate fertilizers. Considerable data have been accumulated since 1925 from studies concerned with (1) the use of phosphate fertilizers, (2) soil factors affecting the availability of phosphorus to plants and the reactions of the fertilizer with the soil, and (3) the development of soil tests relating the extractable phosphorus with the crop response to applied phosphate.

The purpose of this paper is to review the past work, to stress the present state of knowledge of the subject, and to point out the problems needing further investigation. Major emphasis will be given to the importance of the physicochemical reactions occurring between the solid-phase calcium phosphates, the soil solution, and the root membranes, and the nature of the residual phosphates formed from applied fertilizers.

The term "phosphate" will refer to the anions which are formed from the dissociation of orthophosphoric acid or any of its salts.

II. Definition of Alkaline and Calcareous Soils

A calcareous soil is one containing calcium carbonate. Alkaline soils are included with calcareous soils because there are many characteristics common to both soils. In general these soils occur largely in arid regions. An alkaline soil has a pH greater than 7. It should not be confused with an alkali soil, which has a high exchangeable-sodium percentage. Burd (1948) uses the term "calcareous" to describe those soils containing large amounts of exchangeable calcium and limited amounts of kaolinite or hydrated oxides of iron and aluminum, and in which calcium plays a dominant role in determining phosphate solubility. This definition does not conform, however, to those given in soil classifications. There

is no sharp line of distinction between slightly alkaline soils and a neutral or slightly acid soil with respect to phosphorus.

III. The Forms of Soil Phosphorus

Native phosphorus in these soils occurs chiefly in the form of hydroxyapatite, fluorapatite, chlorapatite, wagnerite, and wavellite, and in organic compounds, according to Hibbard (1931). Other minerals of iron and aluminum phosphates undoubtedly exist in the soil, as well as other calcium phosphates and manganese phosphates. In calcareous soils the various forms of calcium phosphate predominate, whereas in acid soils the iron and aluminum phosphates are as important as the calcium phosphates or perhaps more so. The relative importance of iron and aluminum phosphates in alkaline and calcareous soils has not been determined, although McGeorge and Breazeale (1932) imply that the iron and aluminum in calcareous soils may be active in the precipitation of phosphorus in difficultly available forms. McGeorge and Breazeale (1931b) concluded that calcium phosphate in calcareous soils is present as the carbonate-apatite, or $[Ca_3(PO_4)_2]_3 \cdot CaCO_3$. This compound will be discussed more fully under Section V. The amount of phosphorus on the surface of soil particles may be included also as a form of soil phosphorus.

Fuller and McGeorge (1951) report that 31 per cent of the total phosphorus in nineteen Arizona soils was present in organic combinations, and Greb (1952) found 23 per cent organic phosphorus of the total in twenty-three Colorado soils. Very little is known regarding the importance of these organic forms in supplying phosphorus to plants in Western soils.

IV. The Properties of Calcium Phosphates

A review of the known properties of calcium phosphates will be helpful in understanding the application of this information to soil systems. The complexity of the soil system with respect to phosphate behavior has led to investigations of the pure compounds first, in order to more clearly define the soil system. In the case of calcium phosphates, however, an adequate definition of their behavior in aqueous systems is still a very difficult problem. An appreciation of some of these problems should aid in the interpretation of data on the behavior of calcium phosphates in soil systems.

Eisenberger *et al.* (1940) give an excellent review of the basic calcium phosphates, a term they used to include tricalcium phosphate and the apatites. These authors emphasize the precautions one must observe if the system is to be accurately defined.

Starting with $Ca(OH)_2$ and $Ca(H_2PO_4)_2$, Bassett (1917) found that equilibrium was not established in 12 to 14 months. Eisenberger *et al.* (1940) stress that the only certain criterion for equilibrium is to obtain identical results by approaching equilibrium from opposite sides. The use of time-invariance of composition as a criterion of equilibrium is not reliable.

Precipitated calcium phosphates undergo hydrolysis in water. Bassett (1917) found only one composition which is not decomposed by water, i.e., hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, where the mole ratio of CaO to P_2O_5 is 3.3, and the composition P_2O_5:CaO = 0.76. Solids with larger ratios of P_2O_5 to CaO will become richer in CaO when treated with water, whereas those with smaller ratios will become richer in P_2O_5. The only solution which contains P_2O_5 and CaO in the same proportion as is found in the solid phase in equilibrium corresponds to the composition of hydroxyapatite.

Bjerrum (1936) investigated the solubility of calcium phosphates and mentions a troublesome complication due to the formation of a complex ion between calcium and phosphate. Calcium phosphate solutions show a more acid reaction than corresponding sodium phosphate solutions with the same degree of neutralization with respect to phosphoric acid. He postulates a complex, such as $Ca(HPO_4)_2^-$, which seems to have nearly the same acid strength as $H_2PO_4^-$, and is consequently much more acid than the ion $HPO_4^=$. Bjerrum (1936) states that the degree of complex formation is usually less than 10 per cent.

An appreciation of the difficulty in reaching equilibrium with calcium phosphates is evident from the work of Bjerrum (1936), since he reports two values for the solubility product of hydroxyapatite, i.e., one each for equilibrium approached from unsaturated and supersaturated sides.

An important property of the calcium phosphates is their specific surface. According to Hill (1952, personal communication) laboratory preparations of calcium phosphates having the same $CaO–P_2O_5$ ratio may possess specific surfaces ranging from 4 to nearly 150 $m.^2$ per gram, and phosphate rocks appear to have specific surfaces between 1 and 20 $m.^2$ per gram by the method of Brunauer *et al.* (1938). This wide range in particle size of precipitates with identical composition may cause differences in the solubility and solubility product of these calcium phosphates. The solubility of small crystals of a precipitate has been shown to be greater than that of the large crystals by Dundon (1923), May and Kolthoff (1948), and Tourky and El Wakkad (1949).

Eisenberger *et al.* (1940) suggest that the conception of an extended range of solid solutions seems to furnish a more consistent explanation

for the information available in the literature than does the assumption of a definite molecular species with the formula $Ca_{10}(PO_4)_6(OH)_2$. As evidence they cite several cases where precipitates were formed with more than 3.3 moles CaO per mole of P_2O_5, when the solutions contained an excess of limewater. Lorah *et al.* (1929) studied the adsorption of $Ca(OH)_2$ on $Ca_{10}(PO_4)_6(OH)_2$. The data followed the Freundlich adsorption isotherm, and there was no evidence of a reaction between basic calcium phosphate and $Ca(OH)_2$, but the authors were inclined to the opinion that, in addition to adsorption, solid solutions were produced. In the most concentrated $Ca(OH)_2$ solutions approximately one-third of a mole of $Ca(OH)_2$ was adsorbed per mole of basic phosphate.

According to Eisenberger *et al.* (1940), all the calcium phosphates will eventually display X-ray diffraction patterns similar to hydroxyapatite on protracted treatment with water. This seems justification for considering hydroxyapatite as the most stable calcium phosphate, but the conditions under which it is formed must be known in order to be certain of the purity of the final product. When calcium phosphates are repeatedly treated with neutral ammonium citrate solutions, the composition of the precipitate approaches that of hydroxyapatite, according to Jacob *et al.* (1930).

The information pertaining to the preceding discussions was obtained from phase rule, solubility, and solid-phase composition data. When X-ray diffraction methods were applied to the problem, a number of different conclusions were proposed. Trömel and Möller (1932) show that a number of precipitates of different composition gave X-ray diffraction patterns identical with that of hydroxyapatite. Similar difficulties in detecting the presence of carbonate in the apatite lattice have been discussed by Hendricks and Hill (1950). According to Eisenberger *et al.* (1940), when CaX_2 is associated with tricalcium phosphate, its molecules are placed in the crystal lattice, where they cause no detectable difference in the important planes. These observations emphasize again the difficulties encountered in attempting to define the nature of calcium phosphates. Eisenberger *et al.* (1940) conclude that "the apatite lattice is tolerant not only to large variations in the components of the ternary system $CaO—P_2O_5—H_2O$, but also to the inclusion of many other substances in large or small amounts."

Calcium phosphates may be prepared which are either richer in CaO or richer in P_2O_5 than the equilibrium compositions, merely by altering the mode of precipitation, as shown by Hodge *et al.* (1938). Mattson *et al.* (1951) suggest that the calcium phosphates behave as amphoteric colloids and possess an active surface layer, and that their

solubility is intimately related to this condition. The composition of the surface layer depends on the ionic environment. Many of the observed characteristics of calcium phosphates described by Eisenberger *et al.* (1940) suggest the existence of an active surface layer on the crystals, but no mention is made of the amphoteric nature of the precipitates. Electrophoresis measurements by Mattson *et al.* (1951) definitely show this amphoteric property of a precipitated tertiary calcium phosphate. According to Hodge *et al.* (1938), the commercial tertiary calcium phosphates are probably hydroxyapatite with more or less adsorbed phosphate resulting in empirical formulas approaching the composition of $Ca_3P_2O_8$. Bjerrum (1936) also agrees that tertiary calcium phosphates are never precipitated from aqueous solutions, and he states that precipitates of the composition, $Ca_3P_2O_8$ are mixtures of hydroxyapatite and calcium phosphates richer in P_2O_5 than hydroxyapatite.

Some of the known properties of orthophosphoric acid and various calcium phosphates which are pertinent to soil studies are listed in Table I and Table II. The data were taken from Farr (1950). The

TABLE I

SOLUBILITY PRODUCT CONSTANTS OF SEVERAL CALCIUM PHOSPHATES AT 25° C.[a]

Calcium phosphate	*Solubility product constant, pK*
$Ca(H_2PO_4)_2 \cdot H_2O$	1.1436
$CaHPO_4$	6.6616
$CaHPO_4 \cdot 2H_2O$	6.6616
$Ca_{10}(PO_4)_6(OH)_2$	111.8153

[a] Data taken from Farr (1950).

TABLE II

THE PROPORTION OF PHOSPHATE IONS IN SOLUTION PER 100 MOLES OF DISSOLVED PHOSPHATE[a]

pH	*5*	*6*	*7*	*7.2*	*8*	*9*
Moles $H_2PO_4^-$	99.3	94.1	61.3	50	13.7	1.5
Moles $HPO_4^=$	0.6	5.9	38.7	50	86.3	98.4

[a] Calculated from pK_2 value given by Bates and Acree (1943).

solubility product constants for the various calcium phosphates are very useful in determining the effect of pH, soluble salts, and common ions on the solubility of the salts. These solubility products are given in terms of activities. The dissociation constants, K_1, K_2, K_3, for H_3PO_4 represent the three stepwise ionizations of H_3PO_4: i.e.,

$H_3PO_4 = H^+ + H_2PO_4^-$; $H_2PO_4^- = H^+ + HPO_4^=$; $HPO_4^= = H^+ + PO_4^{\equiv}$

At 25° C. these constants are:

$$K_1 = 7.51 \times 10^{-3} \qquad K_2 = 6.34 \times 10^{-8} \qquad K_3 = 4.73 \times 10^{-13}$$

The ratio of $H_2PO_4^-$:$HPO_4^=$ at any pH can be calculated from the relation $[H_2PO_4^-]/[HPO_4^=] = [H^+]/K_2$; i.e., this ratio is 1:1 when the $[H^+]$ equals K_2 or at pH 7.2. Buhrer (1932) reports that these two ions are present in equal concentrations at pH 6.7, using the value for K_2 reported by Abbott and Bray (1909). The value for K_2 given above was determined by Bates and Acree (1943) and is probably more reliable. Since Russell (1950) still used the data reported by Buhrer (1932) to calculate the ratio of $H_2PO_4^-$ to $HPO_4^=$ in relation to pH, it seems worthwhile to present the data calculated from the constant reported by Bates and Acree (1943). These data are shown in Table II. Small amounts of H_3PO_4 and PO_4 occur also at each pH value.

Additional properties of calcium phosphates will be shown in later sections as they pertain to the particular phenomena being described.

V. Reactions of Phosphate with Calcium Carbonate

The solid-phase soil solution processes are dynamic, and information based on studies of equilibrium conditions is necessarily of limited usefulness. The problem is to investigate phenomena in flux rather than systems in their final states, although the equilibrium studies may provide basic steps toward the elucidation of the more complex dynamic equilibria.

In applying the preceding information on calcium phosphates to a calcareous soil, the first problem is to explain the nature of the reactions between $CaCO_3$ and calcium phosphates, including soluble phosphate fertilizers. McGeorge and Breazeale (1931b) noted the depressing effect of solid-phase $CaCO_3$ on the solubility of rock phosphate and attributed the very low solubility of phosphorus in alkaline calcareous soils to the presence of calcium carbonate. The effect was due to the presence of solid-phase $CaCO_3$ as well as the common ion Ca^{++}, since the solubility of phosphate was lower when solid-phase $CaCO_3$ was present than with saturated solutions of $CaCO_3$. The authors state that apparently a reaction occurred between the $CaCO_3$ and the rock phosphate, with the formation of a new compound containing more $CaCO_3$ and having a very low solubility. They concluded that such a reaction occurs in calcareous soils and that the calcium phosphate was present as a carbonate-apatite. These conclusions were based only on solubility measurements, and actual identification of such a compound was not made. Supporting

evidence was cited for the existence of carbonate-apatite in bone. McGeorge and Breazeale (1931b) assumed that a definite molecular species, $[Ca_3(PO_4)_2]_3 \cdot CaCO_3$, containing three moles of tricalcium phosphate to one mole of $CaCO_3$, was formed. Bassett (1917) suggests a stable hydroxyapatite mixed with varying amounts of $CaCO_3$ as being the stable mineral species which can exist in soils.

The effect of $CaCO_3$ on the solubility of rock phosphate or hydroxyapatite can be explained, however, without postulating the formation of another compound. Adsorption of carbonate and calcium ions onto the surface of the rock phosphate crystals would modify the nature of the outer layer of ions by enriching the surface layer with Ca^{++}, and thus decrease the activity of the phosphate ions. The solid-phase calcium carbonate would also adsorb phosphate ions from solution onto its surface, and the relatively higher activity of Ca^{++} from the $CaCO_3$ compared to Ca^{++} from the rock phosphate would lower the activity of the phosphate ions. The nature of the $CaCO_3$ surface may be such that the phosphate ions fit well onto the surface of the crystal, thus causing an additional lowering of the phosphate activity.

Evidence for these conditions is found by analogy with similar reactions in bone and enamel, in recent explanations for the nature of carbonate in bone and francolite, and in the reactions of phosphate ions with $CaCO_3$.

Carbonate is found in bone, enamel, dentine, and in the minerals, collophane and francolite. All these substances have apatite structures by X-ray analysis. Gruner and McConnell (1937) maintain that the carbonate in francolite is present as a part of the crystal lattice, and that the unit cell edges of francolite differ slightly from those of fluorapatite; but Hendricks and Hill (1950) state that X-ray goniometer photographs of francolite crystals are identical with those of fluorapatite. The francolite crystals contained 3 per cent CO_2, which if present as a part of the crystal lattice would be likely to change the diffraction pattern. The question as to whether the crystal lattice dimensions of optically clear francolite crystals differ from those of fluorapatite is not definitely settled.

Logan and Taylor (1938) observed a preferential solution by acid of carbonate in bone. Addition of enough acid to dissolve only 10 per cent of the phosphorus removed 57 per cent of the CO_2. Calcium phosphate precipitates formed at pH 7.0 to 7.4 in solutions containing HCO_3^- ions removed Ca^{++} and $CO_3^=$ ions from solution even though the product $[Ca^{++}] \times [CO_3^=]$ was less than the solubility product of $CaCO_3$. The change in the precipitates during equilibration consisted essentially in an increase in $CaCO_3$ or $Ca(OH)_2$. The composition of the precipi-

tates after 20 days equilibration depended on the composition of the liquid phase in respect to Ca^{++} and anions which may be adsorbed. They regarded the addition of carbonate as a step which took place subsequent to the formation of the main crystal structure.

Crystalline $CaCO_3$ has not been observed in bone by the very sensitive test of its high birefringence, according to Hendricks and Hill (1950). The explanation proposed by them, that the carbonate is adsorbed on the surface of the calcium phosphate crystals rather than being a constituent of the lattice, appears to best explain the observed properties of bone, enamel, and francolite. They proposed that the carbonate groups of enamel and francolite are present on surfaces which are entrapped as the crystallites grow and are surrounded by phosphate. Evidence for entrapped surfaces was obtained by comparing the surface areas of unground and finely ground crystals with bone. Grinding the bone sample had little effect on the surface area, whereas grinding enamel and francolite caused a much larger increase in surface area than would be expected from the decrease in particle size alone. Thus, inner surfaces were exposed on grinding, which were then measurable by the gas adsorption method.

Boischot *et al.* (1950) studied the reaction of dilute phosphate solutions with calcium carbonate. The initial reaction was found to be an adsorption onto the surface of calcium carbonate particles rather than a precipitation of an insoluble phosphate as a separate phase. The amount of phosphorus adsorbed is a function of the fineness of the $CaCO_3$ particles. When the phosphate concentration as $Ca(H_2PO_4)_2$ exceeded approximately 5×10^{-5} *M* phosphorus, at pH 8.3 to 8.5 precipitation did occur.

Similar studies on the adsorption of phosphorus on $CaCO_3$ were conducted in this laboratory and in general confirm the observations of Boischot *et al.* (1950). With dilute solutions of K_2HPO_4, the phosphate adsorbed on the surface of the $CaCO_3$ particles until the phosphorus concentration reached 2×10^{-4} *M*. The data fit the Langmuir adsorption isotherm in the initial stages of the reaction. Conformance of the data to this equation does not constitute final proof that monolayer adsorption is occurring, but it may be considered as strong evidence in favor of such a reaction mechanism. When the phosphorus concentration was greater than 2×10^{-4} *M*, as K_2HPO_4, precipitation began and the equilibrium phosphorus concentration fell below the level found just prior to precipitation.

The preceding discussions indicate the complexity and variety of reactions that can occur between $CaCO_3$ and calcium phosphates. The evidence is quite strongly against the formation of a compound in soils

of the composition indicated by McGeorge and Breazeale (1931b), although a precipitate of unknown composition and with probably a large surface area is formed. In a later study on the availability of residual phosphate in Arizona soils, McGeorge (1942) indicates that soluble phosphates are fixed rapidly as tribasic calcium phosphate and that the final conversion to calcium carbonate-phosphate is a very slow process.

VI. Reactions of Fertilizer Phosphorus with the Soil

A second application of the information assembled on the basic calcium phosphates is to the problem of the nature of the residual phosphate in soils. This phase of phosphate research becomes increasingly important as the use of phosphate fertilizer increases and the residual phosphate accumulates. The nature of the residual phosphate, from a practical viewpoint, is intimately related to the extent of utilization of these forms of phosphate by plants.

The effect of soluble salts, pH, $CaCO_3$, clays, and physical factors on the reactions of soluble phosphate with soil and on the absorption of native and residual soil phosphorus will be shown in this section. An understanding of these phenomena is particularly important to the problem of developing and interpreting soil tests for extractable phosphate.

1. Soluble Salts

The effect of salts on the solubility of native and applied phosphorus is intensified in soils of arid regions because of the greater abundance of soluble minerals and salts. When a neutral salt is added to a saturated solution of a slightly soluble salt, BA, the activity coefficients of the ions B^+ and A^- decrease. This means that the solubility of the salt, BA, increases in solutions of electrolytes having no ion in common with the precipitate, according to Lewis and Randall (1923). This phenomenon is commonly referred to as the "salt effect." Salts having an ion in common with the precipitate decrease the solubility of slightly soluble salts, although the common-ion effect is counteracted to varying degrees by the salt effect. A salt which hydrolyzes to give a change in pH would exert a twofold effect on the solubility of slightly soluble salts, i.e., the salt effect and the change in pH.

The expected effect of salts on the solubility of pure calcium phosphates is clearly indicated above. In soil systems, however, many apparently contradictory results have been reported. McGeorge and Breazeale (1931a) found that NaCl, KCl, and K_2SO_4 all decreased the solubility of rock phosphate and soil phosphate in a calcareous soil. Greaves (1910) found that KCl and NaCl decreased the solubility of rock phos-

phate and soil phosphate but that $NaNO_3$ and K_2SO_4 increased the solubility. Karlsson and Mattson (1940) found that 0.5 *N* KCl solutions increased the solubility of powdered apatite twofold. Apparently, the impurities present in apatite, such as $CaCO_3$, may cause variable results as to the solubility effect of salts. Hibbard (1935) found an increase in solubility with Na_2SO_4 and $(NH_4)_2SO_4$ and a slight depressive effect with K_2SO_4 on the solubility of phosphate in four soils. Calcium and magnesium sulfates depressed the solubility of the soil phosphate on three of the four soils, but increased the solubility on a fourth soil. Wild (1950) has summarized the studies on the effect of salts on phosphate solubility and concluded that there is insufficient knowledge to explain these apparently contradictory results.

Buhrer (1932) points out that alkali chlorides decrease the solubility of phosphate in calcareous soils by interaction with the $CaCO_3$. The salt increases the solubility and hydrolysis of the $CaCO_3$ to produce a higher Ca^{++} ion concentration, which in turn reduces the phosphate concentration. Lehr and Wesemael (1952) presented results with various Dutch soils showing that phosphate solubility decreased with increasing concentration of neutral salts, the depressing effect increasing in the order $Na < K < Mg < Ca$ and being less marked with sulfate than with chloride or nitrate. Different results with pure phosphorus compounds were attributed to the absence of interactions between the salt solutions and the soil. In soil, the cations replace Ca^{++} from the exchange complex, and the Ca^{++} then precipitates the phosphate ions from solution.

Kurtz *et al.* (1946) studied the adsorption of phosphate by Muscatine silt loam in water and in 2 per cent KCl solutions; the adsorption was much greater in the KCl solution. Ericksson (1940) showed by pot experiments and soil studies that KCl caused a decided fixation of the phosphate in soils rich in sesquioxides. Hazeman *et al.* (1950) have identified some of the compounds resulting from the reaction of phosphate with clay as members of an isomorphous series with the general composition $[(H, Na, K, NH_4)_3 (Fe, Al)]PO_4 \cdot nH_2O$. These data are cited as additional evidence that added salts may interact with the soil to give decreases in the solubility of the soil phosphorus. With KCl, the salt may have entered into a specific reaction as a constituent of a precipitated phosphate. The possibility that such reactions may occur in calcareous soils cannot be overlooked in explaining the effect of salts on phosphate solubility. A study of the nature of the interaction of salts with the soil as it affects phosphate solubility would appear to give the most promising answers to the conflicting data noted on the effect of salts on phosphate solubility.

Karlsson and Mattson (1940) found that neutral salts depressed the

solubility of aluminum phosphate at pH values above its isoelectric point (pH 5), but that the salts increased the phosphate solubility at pH values below 5. The phosphate solubility was depressed more with KCl than with NaCl at the isoelectric point and on the alkaline side of the isoelectric point. These data also indicate a specific reaction in the case of KCl.

In some later work Mattson *et al.* (1951) show that similar effects were found with amphoteric calcium phosphates. At low pH values the phosphate solubility is greater in salt solutions than in water. The solubility in water is a minimum at pH 7, which is close to the isoelectric point of the calcium phosphate studied. On the alkaline side of the isoelectric point, the solubility in water is greater than in salt solutions. The pH values of the suspensions were increased by adding NaOH.

The phosphate solubility of the calcium phosphate in the alkaline range was less with NaCl than with KCl, an effect opposite to that found for iron and aluminum phosphates. This result indicates a specific reaction mechanism for Na^+ with calcium phosphate compared to K^+. According to Hendricks and Hill (1950), there is a size limitation for adsorbed ions on the surface of bone crystals, which results in a preferential uptake of Na^+ rather than K^+.

Mattson *et al.* (1951) explain their results on the basis of a Donnan distribution of the ions between the solution and the active surface layer of the calcium phosphate crystals. On the alkaline side where the complex forms a cation atmosphere, the solubility in water (actually a dilute NaOH solution) increases as a result of the Donnan distribution, according to which $[HPO_4^=]_{outside} > [HPO_4^=]_{inside}$. This distribution is suppressed by neutral salts, and leads to a lower phosphate solubility. On the acid side of the isoelectric point, the ion atmosphere is dominated by anions, and the effect of salt is that of anion exchange and a suppression of the activity coefficient, both of which lead to a higher phosphate solubility.

The extent to which such reactions may occur in a calcareous soil is not indicated by Mattson *et al.* (1951). They found that $CaCl_2$ had a suppressing effect on phosphate solubility in all concentrations at all pH values, indicating that precipitation of a calcium phosphate was the dominant reaction. In the presence of free $CaCO_3$ in soils, it is quite likely that the precipitation reactions will remain predominant. Reitemeier (1946) studied the effect of dilution on the soluble salts in several calcareous soils. Both nitrate and chloride ions consistently showed a "negative adsorption," or a decrease in concentration with increase in dilution, which can be explained on the basis of a Donnan distribution. The phosphate ion, however, consistently increased in con-

centration with increases in dilution, an effect which Reitemeier (1946) attributes to solution of "insoluble" phosphates by additional water, dilution of soluble calcium salts, and anion replacement by hydroxyl ions. Thus, the magnitude of a Donnan distribution of phosphate ions in a calcareous soil is quite likely to be small, but additional investigations are needed to determine the actual effect.

Alkaline soils saturated largely with calcium may be expected to show, to a greater extent than the calcareous soils, some of the effects of a Donnan distribution of phosphate ions of the type indicated by Mattson *et al.* (1951). This is a problem certainly in need of further investigation.

2. *Effect of Salts on Root Membranes*

If all of the effects of salts on the solubility of phosphate in a given soil were known, the system, with respect to the plant uptake of phosphate, would be defined only in part. Mattson *et al.* (1949) studied the effect of electrolytes on the uptake of phosphate ions by peas on a clay soil, pH 6.96. The chloride and nitrate salts of Na, K, Mg, and Ca all increased the total phosphorus content of the peas and, in particular, the phytin content increased. Addition of $NH_4H_2PO_4$ also caused a marked increase in total phosphorus content and in phytin-P. When 1 equivalent of $CaCl_2$ per $m.^2$ (506 lb. $CaCl_2$ per 2×10^6 lb. soil, or 0.025 per cent salt) was applied in addition to the $NH_4H_2PO_4$, a further increase in total phosphorus content and phytin-P occurred. The authors had expected that the $CaCl_2$ would counteract the positive effect of the $NH_4H_2PO_4$, by decreasing the solubility of phosphate in the soil. Nitrate uptake was likewise favored by the salts.

Mattson *et al.* (1949) state that the mechanism involved can be explained by the Donnan distribution of ions between the soil solution and the root membrane. Regardless of which mechanism, or other possible explanations, the results of Mattson *et al.* (1949) emphasize that the total salt effect on the phosphate uptake by plants is composed of at least two important factors: (1) the effect on phosphate solubility in the soil, and (2) the effect of the salt on the root membranes. In this particular experiment, the latter effect more than compensated for the reduced phosphate solubility in the soil.

The question arises as to whether these salt effects on the soil solution and the root membrane occur in alkaline calcareous soils. Mattson *et al.* (1949) state that some nutrient solutions, e.g. the Hoagland solution, are too concentrated for these studies and the salt effect is already so great that an extra addition of salt produces very little effect. The amount of $CaCl_2$ added by Mattson *et al.* (1949) is somewhat less than

the soluble salt content of many slightly saline soils, but within the concentration range of many other soils in arid regions. Therefore, the type of effects noted by Mattson *et al.* (1949) could be expected on some alkaline calcareous soils, but in moderately saline soils, salt additions would be likely to show little effect.

According to Mattson *et al.* (1949), whether the net effect of salt will result in an increase or a decrease in phosphate uptake depends upon several factors, such as the composition of the soil, the nature and concentration of the salt, and the pH.

McGeorge (1939) studied the effect of additions of $MgSO_4$ and concentrated superphosphate on several Arizona soils. Rye and Sudan grass showed a slight increase in absorption of phosphate as a result of the $MgSO_4$, whereas cotton absorbed less phosphate. The initial salt levels were not given.

The variations in content of salts normally present in arid soils may be exerting effects on phosphate uptake by plants to a greater extent than is generally assumed. In studies relating soil moisture levels to phosphate uptake, for example, the effect of moisture levels on salt content, with the subsequent effects on phosphate uptake by the plants, should be considered as one of the indirect effects of the various moisture levels. Reitemeier (1946) studied the effect of dilution on the soluble ions in soils. Those soils containing slightly soluble salts such as $CaSO_4$ and $CaCO_3$ showed an increase in soluble salts on dilution, except for NO_3^- and Cl^-.

Wadleigh and Richards (1951) have reviewed the subject of nutrient accumulation in plants at various levels of soil moisture supply. They state that most experimental evidence shows that, for a given level of fertility, decreasing soil moisture supply is associated with a definite increase in nitrogen content of the plant tissue, a definite decrease in potassium content, and a variable effect upon the content of phosphorus, calcium, and magnesium. The effect of moisture on phosphorus content is far less consistent than that observed for nitrogen and potassium. They attribute this to variations in the fixing power of soils for phosphate as conditioned by soil moisture content. In addition to variations in fixing power for phosphate, the possible effects on phosphate uptake by the plants of variations in soluble salts, as related to soil moisture content, should also be considered.

3. *Effect of pH*

The effect of pH on phosphate solubility can be discussed adequately only when the combined effects of pH on the plant roots and the soluble phosphate are known. McGeorge (1939) indicates that in alkaline cal-

careous soils the phosphate solubility increases above pH 8.5, is at a minimum within the range 7.6 to 8.5, and increases again below pH 7.6. Burd (1948) shows a curve for the solubility of phosphate in relation to pH for a calcareous soil. A minimum solubility is indicated near pH 7.0, with increasing solubility at higher and lower pH values. Gardner and Kelley (1940) show solubility curves for soil phosphate in various Colorado soils. All the curves were of the same general type, with a minimum solubility near pH 7 to 8, and an increasing solubility at higher or lower pH values.

If the pH is raised by additions of NaOH, the solubility of the calcium phosphate increases, but if $Ca(OH)_2$ is added to increase the pH, the solubility of the calcium phosphate decreases as a result of the common-ion effect.

The results of various investigations agree generally that phosphate solubility in calcareous soils is at a minimum in the range of pH 7.0 to 7.5, and increases with either an increase or decrease in pH from this range. With pure systems, or precipitated calcium phosphates, the results are somewhat different.

Gaarder (1930) found that the solubility of phosphate in a calcium phosphate suspension reached a minimum at pH 6.5, with little change up to pH 11. Benne *et al.* (1936), using techniques based largely on those of Gaarder (1930), found a minimum solubility for calcium phosphate at pH 7.5 and no increase in phosphate solubility up to pH 12. Both studies were based on precipitates obtained by mixing soluble calcium salts with dilute solutions of H_3PO_4. Teakle (1928) added $CaCl_2$ to NaH_2PO_4 solutions and found a decreasing solubility of the precipitated calcium phosphate from pH 6 to 10.

When Benne *et al.* (1936) added $CaCO_3$, as a source of calcium instead of $CaCl_2$, to the dilute H_3PO_4 solutions, the phosphate solubility curve showed a marked difference in relation to pH. The pH was varied by additions of HCl or NaOH to the suspensions. A minimum solubility occurred at pH 7.5; then the phosphate solubility increased as the reaction increased to pH 10, followed by a decrease. The authors attribute this effect to the slight solubility of the $CaCO_3$ and possibly to the effect of the Na^+. When NaOH was added with $CaCl_2$ and H_3PO_4, however, complete precipitation occurred at pH 7.4, and no increase in soluble phosphate was found up to pH 12. Both carbonate and bicarbonate ions were present in these mixtures, and the authors state that when $CO_3^=$ ion was present there was a tendency toward supersaturation of the solutions with respect to calcium and phosphate.

The most interesting feature of the data of Benne *et al.*, (1936) where $CaCO_3$ was used is that the phosphate solubility curve is very

similar to that found for soil phosphate in a calcareous soil, as shown by Burd (1948). Evidently the solubility of phosphate in calcium phosphates in relation to pH is not the same in the presence of $CaCl_2$ or CaO as with $CaCO_3$. A possible explanation of these differences may be found in the repression of the Ca^{++} activity due to the common-ion effect of the $CO_3^{=}$ in the presence of solid-phase $CaCO_3$. Benne *et al.* (1936) added H_3PO_4 to the $CaCO_3$ first, followed by NaOH, so the system contained HCO_3^- and $CO_3^{=}$. As the pH increases, the $CO_3^{=}$ increases and suppresses the Ca^{++} ion activity, which allows a higher activity of $HPO_4^{=}$ in solution.

Gardner and Kelley (1940) showed that 1 per cent K_2CO_3 solutions increased the solubility of phosphate in calcareous soils and indicated that this increase was due largely to the solution of a calcium phosphate rather than iron or aluminum phosphates. They point out that the CO_3 reduces the Ca^{++} to very low values. The solubility of phosphate in the slightly acid range is closely correlated with the solubility in the highly alkaline range for soils of similar composition. This indicates that the dissolving action of slightly acid and also alkaline solutions is upon similar forms of calcium phosphates.

The combined effect of pH on phosphate solubility in soil and on the root membranes was indicated previously. According to McGeorge (1939), the soil reaction is the principal limiting factor in phosphate availability in Arizona soils and much stress is given to the importance of CO_2 in modifying the soil reaction. Whitney and Gardner (1942) studied the pH of soils as a function of CO_2 pressure and found that the pH is approximately a straight-line function of the log of the CO_2 pressure in the range from 0.0003 to 1 atmosphere at constant moisture. Small changes in CO_2 pressure cause comparatively large changes in pH within the range of low CO_2 pressures normally found in soils.

McGeorge (1932) showed that in nutrient solutions the phosphate absorption by wheat plants began to decrease at pH 8 compared to pH 7, and that a marked decrease occurred at pH 9. He attributed the entire effect on the plant of increasing pH to a decrease in $H_2PO_4^-$.

Pratt and Thorne (1948) show similar results for tomatoes, but indicate that a physiological change in the root membranes to give a decreased permeability to phosphate seems a more logical explanation of their study. The decrease in absorption was not serious until pH 8 was exceeded. Arnon *et al.* (1942) studied the effect of pH in relation to absorption of phosphate by tomato, lettuce, and Bermuda grass. A marked reduction occurred at pH 9, and absorption at pH 8 < pH 7. Arnon *et al.* (1942) state that their findings are not entirely consistent with those of McGeorge (1932) and suggest that the influence of OH^-

on phosphate absorption should be considered also. Since anions appear to be absorbed by plant roots in exchange for OH^- or HCO_3^-, as indicated by Overstreet and Dean (1951), an increasing OH^- concentration would be expected to decrease the rate of exchange of $H_2PO_4^-$ on the membrane, if a reversible reaction is assumed.

4. Effect of Calcium Carbonate

The depressing effect of $CaCO_3$ on the absorption of phosphate by plants is due to a decreased solubility of soil phosphate and to the tendency of $CaCO_3$ to maintain a high pH, according to McGeorge (1939). Attempts to correlate the $CaCO_3$ content of soils with crop response to fertilizer have shown variable results. Work by McGeorge (1939), Hibbard (1935), Ensminger and Larsen (1944), Smith (1948), and Hockensmith *et al.* (1933) has shown that, within the range of 1 to 4 per cent lime, phosphate absorption by plants is roughly inversely related to the lime content of the soil. When the lime content is greater than 4 per cent, the correlation is very poor, but usually the crop response is greater on high lime soils.

Soluble nitrogen fertilizers, such as NH_4NO_3 and $(NH_4)_2SO_4$, added to soils cause a decrease in pH, particularly in localized areas. If the soil is light-textured, or has a low buffer capacity and contains small amounts of $CaCO_3$, these nitrogen fertilizers may increase the absorption of phosphate by plants and also decrease the rate of conversion of the phosphate to less-soluble forms.

Thorne (1946) studied the effect of varying amounts of $CaCO_3$ added to a clay-nutrient system on the growth and composition of plants. The $CaCO_3$ decreased the water-soluble phosphate and the concentration of phosphorus in tomato plants was approximately inversely proportional to the concentration of $CaCO_3$. The growth of tomatoes was not affected appreciably when the ratio of clay to $CaCO_3$ was 20:1 or 10:1, but decreased rapidly when the ratio changed from 5:1 to 1:1. Barley seemed to be little affected in growth over a wide range of concentration of $CaCO_3$, thus showing a crop difference in sensitivity to the effect of $CaCO_3$.

Some of the possible reactions of soluble phosphates with $CaCO_3$ were indicated previously from the work of McGeorge and Breazeale (1931b), McGeorge (1939), and Boischot *et al.* (1950). These reactions include conversion to a less-soluble precipitate of a calcium phosphate, with the $CaCO_3$ furnishing the calcium, and followed by excess Ca^{++} and $CO_3^=$ being adsorbed onto the surface of the calcium phosphate crystals. These crystals probably grow on the surface of $CaCO_3$ particles, since the initial phase of the reaction was shown by Boischot *et al.*

(1950) to be an adsorption of phosphate onto the surface of the $CaCO_3$ particles. As this adsorption layer increases in thickness, crystal nuclei of a calcium phosphate form and precipitation proceeds according to the mass action law. The activity of phosphate and calcium remaining in solution after precipitation would depend upon the solubility product constant of the particular calcium phosphate species formed. Initially this compound is likely to be dicalcium phosphate, but in the presence of $CaCO_3$ it would slowly change to calcium phosphates richer in calcium and to a lower solubility of phosphate.

The time required for conversion of the dicalcium phosphate to less soluble forms is an important factor governing the rate of absorption of the residual phosphate, assuming that a less-soluble form of phosphate is more slowly absorbed by the plant. MacIntire and Shaw (1934) made a slurry of dicalcium phosphate and limestone. The slurry was wetted each week for ten months, then allowed to dry for two months. After one week, 30 per cent of the dicalcium form had changed to a less-soluble form, and 60 per cent conversion was found after a year. Russell (1950) suggests that two to three years may be required in soils before dicalcium phosphate is fully converted to less-soluble forms. Dicalcium phosphate is not ordinarily applied alone to soils, but rather in close association with soluble salts, which may well decrease the rate and amount of conversion to less soluble forms.

5. *Reaction with Clays*

A number of investigations have shown that a calcium-saturated clay adsorbs more phosphate than a sodium-saturated clay (see Naftel, 1936; Ravikovitch, 1934; Scarseth, 1935; and Davis, 1943). Allison (1943) found this difference on Miami, Cincinnati, and Frederick colloids, and Pratt and Thorne (1948) showed the same effect for a montmorillonite-type clay. There is general agreement among these studies that above pH 6.5 precipitation of a calcium phosphate occurs as a separate phase, so in alkaline soils this reaction mechanism is probably dominant. The initial phase is probably a direct precipitation from Ca^{++} and $HPO_4^{=}$ in solution, proceeding when the solubility product for $CaHPO_4$ is exceeded. Subsequent enrichment of the precipitate with more calcium is likely to occur. This reaction mechanism is somewhat different from that of phosphate with $CaCO_3$, where the calcium phosphate crystals appear to grow on the surface of the $CaCO_3$, after the initial monolayer adsorption. With dilute phosphate solutions on a calcium-saturated clay, it seems likely that phosphate could be held in a monolayer, or diffuse ionic atmosphere layer, but as such it would be rapidly exchangeable and readily absorbed by plants. Crystal nuclei of

$CaHPO_4$ would not be likely to form and grow on the surface of a calcium-saturated clay as readily as they would on the surface of $CaCO_3$ particles because of this difference in solubility of the initial monolayer. These differences in reaction mechanisms may be reflected in the size of the particles formed from residual phosphate; i.e., they would be smaller on $CaCO_3$, although no information is available to decide this question at present. Russell (1950) indicates that when precipitation occurs, presumably as $CaHPO_4$, with exchangeable calcium on clays, the crystals are adsorbed on the surface of the clay particles, but that this adsorption could take place subsequent to the initial precipitation from the ions in the intermicellar solution.

In the presence of calcium carbonate the reaction mechanism is probably a combination of the individual reactions indicated previously for phosphate with $CaCO_3$ and a calcium-saturated clay. The end product in this case, however, is likely to be similar to the calcium phosphate reaction with $CaCO_3$, since this product is less soluble. Boischot *et al.* (1950) state that the calcium phosphate precipitates partially redissolve in the soil solution, and then become adsorbed on the surface of the $CaCO_3$ particles. This process would lead to a distribution of the residual phosphate over a large surface area in the soil.

6. Effect of Soil Physical Properties on Phosphate Availability

A thorough review of the effect of soil physical properties on nutrient availabilty is given by Page and Bodman (1951). Variations in physical factors from one soil type to another, or from one season to the next, may greatly modify the application of soil tests for extractable phosphorus. The extent of the root system, which is closely related to soil aeration and mechanical impedance, is an important factor determining whether or not the plant responds to phosphate fertilizer.

The general practice of drying soil samples before the analysis for soluble phosphate may involve considerable errors, since Wiklander *et al.* (1950) have shown that the ratio of phosphate solubility in the moist soil to that found in the dried soil can vary a great deal from soil to soil. These factors further illustrate the complexity of the problem of accurately assessing the phosphate fertility level of soils.

VII. Some Properties of Residual Phosphate in Soils

In most studies on the retention of soluble phosphate by soils, major emphasis has been given to the conversion of the soluble phosphate to less-soluble forms, often with the implication that this process reduces the amount of phosphate that plant roots can absorb. On calcareous soils the precipitated calcium phosphates were believed to be more slowly

absorbed than freshly added water-soluble phosphates, with much of the precipitated phosphate being fixed inside the crystal particles. The extent to which plants can utilize these residual forms of phosphate is one of the most important problems in soil management practice. The evidence indicates that the residual value of applied phosphates is the greatest in neutral soils, somewhat less in alkaline calcareous soils, and the least in acid soils, particularly those high in sesquioxides and kaolinite, as indicated by Murphy (1939), Williams (1949), and Russell (1950).

Stanberry (1948) studied the residual value of applied phosphates in a calcareous Sagemoor fine sandy loam and found a residual effect to alfalfa of a moderate application of phosphate fertilizer after five years. Lewis *et al.* (1950) indicate that crops utilize a portion of the residual phosphate on Idaho soils. Russell (1950) reports a residual response by alfalfa on neutral and acid soils for three years following an application of 100 pounds P_2O_5 per acre. Volk (1945) found that cotton responded to residual phosphate, from five previous annual applications of 60 pounds P_2O_5 per acre as superphosphate, for a period of seven years. Williams (1950d) found crop responses to 200 pounds P_2O_5 per acre for two years following the application. Pot measurements of the residual value of field applications indicated that the efficiency of one-year-old residues was 50 per cent as great as that of freshly added superphosphate. Welch and Nelson (1952) showed that the phosphate fertility level of North Carolina soils has greatly increased as a result of heavy phosphate applications on potato-, tobacco-, and cotton-producing areas. Peterson and Paschal (1951) reviewed the fertilizer work in the Western States and stated that a major deficiency in the present fund of information was the lack of data on the residual effects of the phosphate fertilizers.

Lewis *et al.* (1950) indicate that the time of application of superphosphate on a calcareous soil is not important; this is in agreement with Williams' (1950d) data on acid Scottish soils. Sugar beet farmers in the West commonly apply superphosphate in the fall or spring, and no appreciable differences in the yield of sugar beets in relation to time of application of superphosphate was found in experiments reported by Tolman (1950). No critical field studies have been published to show the relative efficiency of the residual phosphate to crops after the first year of application to calcareous soils. The utilization of applied phosphate in one crop on calcareous soils was shown by Olsen *et al.* (1950) to be less than 10 per cent; considerable amounts of residual phosphate may thus be expected to accumulate under good soil management practices.

The results on crop responses to residual phosphate, except as noted for certain acid soils, indicate that the forms of residual phosphate may be absorbed by plants in varying degrees, and, in general, the amount absorbed decreases with time. Plants often show a more marked response to phosphate during the early stages of growth. Therefore, relatively small, frequent applications of phosphate would appear to supply the readily absorbable phosphate when needed, and as the root system expands, more use will be made by the plant of the residual and native phosphate. Such fertilizer practices would appear to make the most economic use of phosphate fertilizers.

VIII. The Relationship of Surface Phosphate to Plant-Available Phosphate in Soils

1. Factors Involved and Experimental Techniques

The utilization of residual phosphates by plants should be related not only to the solubility of the retained phosphate but also to the amount of phosphate surface exposed to the soil solution. If it is assumed that the soil solution is the sole source of phosphate for plants, it would be necessary for the soluble phosphate to be renewed many times during the growing season. Stout and Overstreet (1950) estimate the renewal of soil solution phosphate on the average of ten times per day for a greenhouse experiment, and much higher values during periods of rapid growth.

Burd (1948) indicates that the surface of phosphate-carrying particles is probably the most important factor in determining phosphate solubility in soils, particularly in the short time involved in the transfer of such ions from the solid phase to the soil solution or a plant root surface. Because of surface tension effects, and possibly others, the solubility of small crystals of a given solid is higher than that of the large crystals, according to Dundon (1923). Kolthoff and Sandell (1943, p. 104) state that amorphous precipitates show a much greater solubility than large crystalline precipitates. These observations show the need to study the amount of phosphate on the surface of particles as well as its solubility. Hazeman *et al.* (1950) indicate that the failure to observe X-ray patterns for precipitated iron and aluminum phosphates in soil is due to their very finely divided state.

Boischot *et al.* (1950) did not employ radiophosphorus to determine the amount of phosphate on the surface of the $CaCO_3$ particles (see Section V). McAuliffe *et al.* (1947) measured the amount of phosphate on the surface of soil particles, and Olsen (1952a) followed a similar technique to measure the amount of phosphorus on the surface of

hydroxyapatite and rock phosphate crystals. Wiklander (1950) used P^{32} to study the mechanism of phosphate sorption and desorption in soils. On a calcareous Marsta subsoil the P^{32} equilibrated with 87 per cent of the added phosphate in 84 hours. The procedure used to obtain the data reported here on "surface phosphate" was described by Olsen (1952b). The values for surface phosphate in soils were obtained after allowing the P^{32} to equilibrate with P^{31} for 60 hours. The amount of solution phosphate present after 60 hours was added to the values for surface phosphate. Usually the solution phosphate is less than 10 per cent of the surface phosphate, but in some soils, such as the Tripp fine sandy loam, the solution phosphate is almost as large as the surface phosphate.

The reason for selecting a 60-hour equilibration time for P^{32} with P^{31} is to include all of the readily exchangeable phosphate on the surface of the particles, and yet minimize the complicating secondary reactions which occur, such as penetration of the P^{32} onto surfaces inaccessible to the solution and possibly to phosphate layers beneath the surface layer.

Further evidence of a monolayer adsorption of phosphate on $CaCO_3$ is obtained by the use of P^{32}, as shown by the data in Table III. The

TABLE III

EQUILIBRATION OF P_{32} WITH VARYING AMOUNTS OF ADSORBED PHOSPHATE ON $CaCO_3$. VALUES IN MICROGRAMS PHOSPHORUS PER GRAM OF $CaCO_3$

P^{31} added	*P^{31} adsorbed*	*P^{31} equilibrated with P^{32}*[a]
46.3	25	24.4
154	55	55.7
13,400	7,000[b]	2,270

[a] After 72 hours equilibration time.

[b] Precipitation of a calcium phosphate occurred.

added P^{32} will equilibrate with all the phosphate adsorbed in the initial reaction, but only 32 per cent of the phosphate removed by precipitation equilibrated with the P^{32}.

Similar results were found on two soils to which varying amounts of phosphate had been added and time allowed for equilibration, as shown in Table IV. The P^{32} added equilibrated with essentially all the phosphate adsorbed from solutions of low concentration, but with only 47 per cent of that adsorbed from higher phosphate concentrations.

Evidence is shown in Table V, from an experiment conducted under more normal field conditions, that the residual phosphate in soils is present largely as surface phosphate initially, and then with time grad-

TABLE IV

EQUILIBRATION OF P^{32} WITH VARYING AMOUNTS OF ADSORBED PHOSPHATE ON SOILS. VALUES IN MICROGRAMS PHOSPHORUS PER GRAM OF SOIL

Soil	*Lime per cent*	*P^{31} added*	*P^{31} adsorbed*	*P^{31} equilibrated with P^{32}*
Declo loam	6.0	44.2	29.4	28.1
		205	99.6	93.6
Gaylardt (farm)	1.2	44.2	34.3	30.1
		205	115	110
		3,280	1,040[b]	492

[a] After 96 hours equilibration time.
[b] Precipitation of a calcium phosphate occurred.

TABLE V

EFFECT OF TIME AND MOISTURE ON THE AMOUNT OF SURFACE PHOSPHATE FOUND IN A FERTILIZED FORT COLLINS LOAM

P_2O_5 added, pounds/acre	*Time of standing, days*	*Surface and solution P_2O_5, pounds/acre*	*Increase in surface and solution P_2O_5*	*Increase P_2O_5 added* $\times$ *100*	*Yield, grams/pot*
0	0 (dry)	75	...	..	3.2
0	85 (wet)	82	...	..	1.9
40	0 (dry)	109	34	85	7.1
40	85 (wet)	100	18	45	3.4
200	0 (dry)	221	146	73	10.4
200	85 (wet)	188	106	53	9.6

ually decreases. The fertilizer was mixed with a Fort Collins loam and water added to bring the soil near the moisture equivalent. The water lost through evaporation was replaced every few days. A similar set of samples was left to stand in the air-dry condition. The rate of decrease in surface phosphate between 0 and 85 days is not shown, but the indications are that the reaction proceeds very rapidly at first After 60 hours, i.e., reaction time for P^{32} equilibration, 85 and 73 per cent of the total P_2O_5 added was measurable as surface and solution phosphate for the 40 and 200 pounds P_2O_5 per acre rates, respectively.

These data do not prove that in the initial phases of phosphate adsorption the phosphate is adsorbed as a monolayer, since the extent to which P^{32} would equilibrate with several layers of adsorbed phosphate is not known. When precipitation occurs, however, the P^{32} equilibrates with only 20 to 50 per cent of the precipitated phosphate, depending on the size of the new crystals formed.

A new method for measuring the amount of available phosphate in

a soil was suggested by Fried and Dean (1952; see Chapter II). Briefly, the method involves the application of phosphate fertilizer containing P^{32} to soil (preferably in a greenhouse pot) and determining the percentage of the phosphorus in the plant derived from the fertilizer. From the equation, $A = B[(1-y)/y]$, where A equals the amount of phosphate in the soil as available as the applied phosphate, B equals the rate of applied phosphate, and y equals the proportion of phosphorus

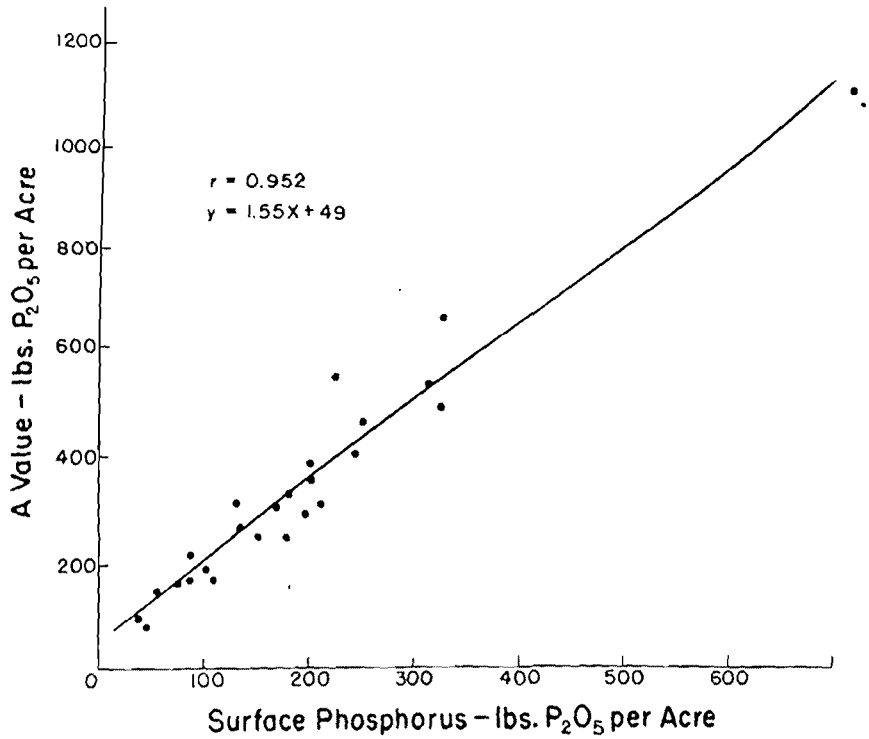


FIG. 1. Relationship between surface phosphorus and A values on 25 soils (uniform wheat experiment, 1951).

in the plant derived from the fertilizer, the amount of available phosphorus, A, can be calculated. This method has been applied to the problems of measuring the plant-available phosphate in native soils and from applied fertilizers.

The relationship between A values and the amount of surface phosphate in two experiments are shown in Figs. 1 and 2. The data in Fig. 1 were obtained from twenty-five soils from various Western States and Canada. Seven of these soils had pH values below 6, and seven contained $CaCO_3$ with pH values over 7, with the rest intermediate in pH values. The A value was determined in a greenhouse experiment at

Beltsville, Maryland, by M. Fried. The data in Fig. 2 were obtained from ten plots, each selected from long-time rotation plots at Fort Collins, Colorado; Huntley, Montana; and Scotts Bluff, Nebraska. At each location five plots were unfertilized, and five had received either manure or phosphate for a period of years. The values for these soils are the surface phosphate plus the solution phosphate found at near equilibrium. The combination of the two values showed a higher correlation

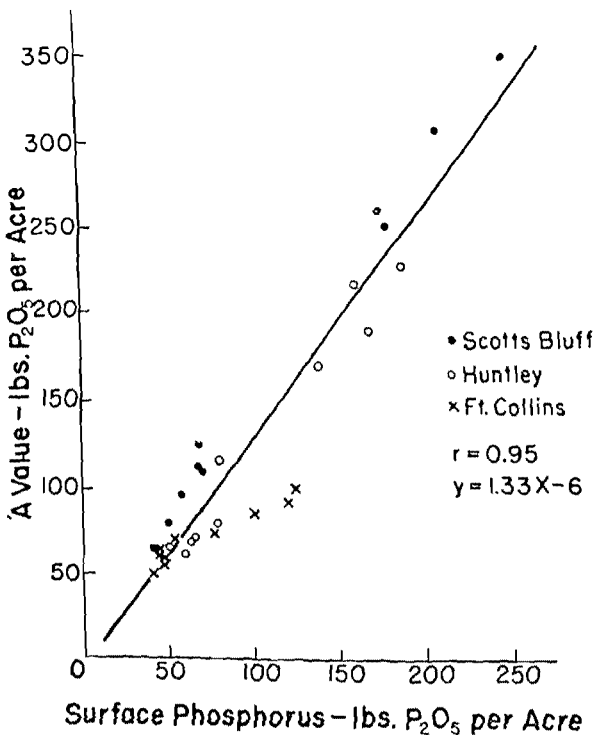


FIG. 2. Relationship between surface phosphorus and *A* values on soils from long-time rotation plots.

with *A* values than was found with surface phosphate alone. The *A* values were determined in a greenhouse experiment. All three soils contain lime. The differences in *A* values are due to the amount of residual phosphate present.

The data in Figs. 1 and 2 clearly show a close relationship between the *A* value, or plant-available phosphate, and the amount of surface phosphate. Furthermore, the correlation coefficient is 0.952 for a rather wide variety of soil types and conditions. These data suggest that the measurement of surface phosphate may be useful in the study of the reactions occurring when a fertilizer is applied to a soil and in developing a better soil test for extractable phosphate.

2. *Application to Soil Tests for Extractable Phosphate*

Correlations of *A* values with various chemical extractants for the group of twenty-five soils is shown in Table VI. The low correlations found with water- and carbon dioxide-soluble phosphate illustrate that the relationship between these values and the *A* value varies considerably from one soil type to another. Within a given soil type, or soil types

TABLE VI

CORRELATIONS OF *A* VALUES ON TWENTY-FIVE WESTERN SOILS (UNIFORM WHEAT EXPERIMENT, 1951) WITH SOLUBLE PHOSPHORUS BY VARIOUS METHODS AND WITH SURFACE PHOSPHORUS

Method or extractant	*Correlations*	
	r	r^2
CO_2	0.128	0.016
HOH	0.411	0.169
Bray	0.786	0.618
$NaHCO_3$	0.860	0.740
Surface phosphorus	0.952	0.905

TABLE VII

PHOSPHATE LEVELS FOUND BY VARIOUS METHODS IN RELATION TO SOIL TYPE AND TREATMENT

Soil type	*Treatment*	*Extractable P*		*Surface + solution P, p.p.m.*	*A value, p.p.m.*
		CO_2-soluble, p.p.m.	*Water-soluble, p.p.m.*		
Fort Collins loam	Check	0.94	0.46	10.1	12.8
	Phosphated	2.36	1.44	21.0	18.4
Pryor silty clay loam	Check	1.83	1.11	14.7	17.3
	Manure	5.28	3.56	31.6	31.6
Tripp fine sandy loam	Check	6.15	1.83	12.7	20.3
	Manure	26.80	8.85	38.8	56.6

closely related with respect to phosphate nutrition, both of these methods will show very high correlations with *A* values. With the long-time rotation plots where phosphate levels were induced as a result of rotation practices and differences in applied phosphate, these two methods are equally as good as the surface phosphate in distinguishing differences in plant-available phosphorus at a given location. The variability

of the extractable phosphate level on different soil types, however, is much greater for the CO_2- and water-soluble phosphate than for the surface plus solution phosphate, as shown in Table VII. All of the check plots gave a yield response to applied phosphate in field experiments.

Evidently, the soil factors affecting the solubility of phosphate in CO_2-saturated water and in water alone are not the same from one soil

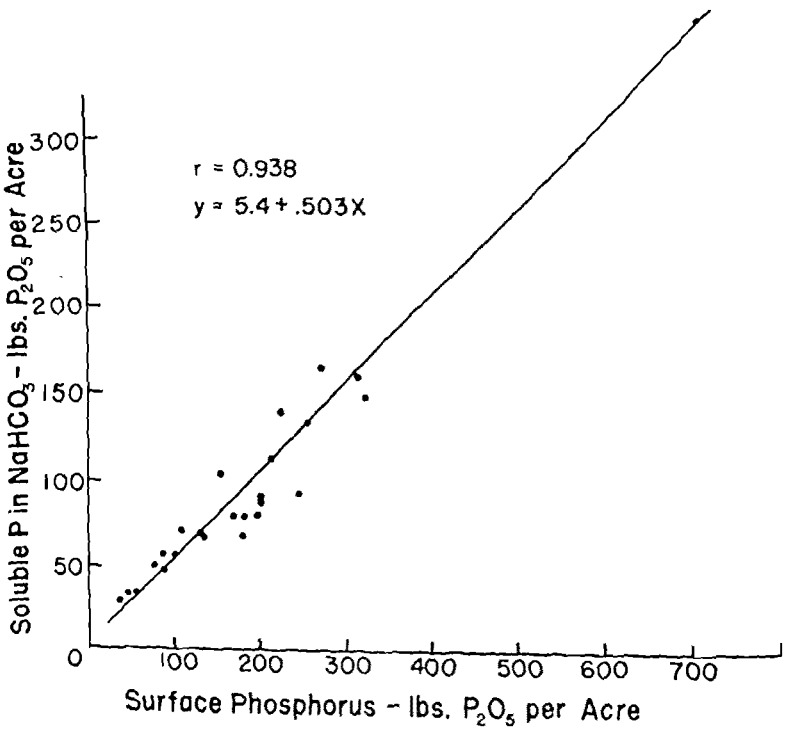


FIG. 3. Relationship between surface phosphorus and phosphorus soluble in 0.5 *M* sodium bicarbonate on twenty-five soils (uniform wheat experiment, 1951).

type to another. Therefore, when these tests are to be employed, a different set of standards must be determined whenever an appreciable change in the phosphate solubility is found with changing soil conditions. In general, a greater degree of success with soil tests for phosphate has been found in areas where such factors as soil type, salinity, climate, and crop are sufficiently alike to permit the establishment of useful correlations between the chemical test and crop growth. The most difficult problem is not the measurement of phosphate levels on the very fertile nor the very infertile soils but the measurement of those lying in between these two extremes.

The measurement of surface phosphate is much less affected by variations in soil factors than is that of the CO_2- or water-soluble phos-

phate. Thus, a method for extractable phosphorus which tends to remove the surface phosphate would logically appear to give a high correlation with *A* value for a wide variety of soil types. An experimental method now showing promise in this respect is the phosphate extractable in a 0.5 M solution of $NaHCO_3$ at pH 8.5. The relationship of this method to the surface phosphate is indicated in Fig. 3 for the group of twenty-five soils mentioned previously. The correlation coefficient was 0.86 for the comparison between *A* value and $NaHCO_3$-soluble phosphate.

Burd (1948) attempted to show the importance of the surface of phosphate-carrying particles by use of a technique designated as "contact equilibrium" and by using wide ratios of soil to solution. This method gave a high correlation with the yield response of oats due to phosphate fertilizer.

IX. Increase in Surface Phosphate from Residual Phosphate in Soils

The close relationship between *A* values and surface phosphate (Fig. 2) for the long-time rotation plots clearly shows the usefulness of these methods in evaluating the residual phosphate in a soil. These methods can probably be adapted to similar studies on acid and neutral soils likewise. Some very useful information concerning the nature of the residual phosphate can be obtained through measurements of the relative amounts of surface phosphate in the unfertilized and the fertilized soils.

The amount of surface phosphate in the check plot of four soils was found to be less than 3 per cent of the total phosphorus in the soil. This value is the same order of magnitude for the surface phosphate in a rock phosphate sample, as determined by Olsen (1952a), which had a surface area of 13.9 $m.^2$ per gram. As the particle size decreases, the amount of surface phosphate to the total increases. The amount of surface phosphate formed in soils fertilized under field conditions is shown in Table VIII. In the Fort Collins loam, 244 pounds of P_2O_5 per acre had been added to the soil over a period of ten years in four applications. During this period the crops have removed an estimated 42 pounds of P_2O_5 from the applied fertilizer, assuming an average of 10 per cent phosphorus in the plant derived from the fertilizer, which leaves approximately 200 pounds of P_2O_5 as residual phosphate. Determinations of the surface phosphate in the unfertilized and fertilized plots show a difference of 61 pounds of P_2O_5 per acre (average of four replications). Based on the amount of residual phosphate remaining in the soil, this means that 30 per cent of the residual phosphate is still retained on the surface of the soil particles. Corresponding figures

for the other three soils are 31.4, 19.6, and 26.8 per cent. respectively, for the Tripp fine sandy loam, Pryor silty clay loam, and Sagemoor fine sandy loam. The first two soils had received an average of 6 and 4 tons of manure per year, respectively, from 1912 to 1950. Samples were taken in 1951. The residual phosphate on these two soils was measured by the differences in total phosphorus. The organic phosphorus content did not change appreciably as a result of the manuring treatments. The Sagemoor fine sandy loam had received an annual application of 15 tons manure from 1932 to 1943, and an average of 6.4 tons from 1922 to 1931, according to Stanberry (1948). The total phosphorus analyses were taken from Stanberry (1948) for this soil.

TABLE VIII

RELATIONSHIP OF SURFACE PHOSPHATE TO TOTAL PHOSPHORUS IN FERTILIZED AND NONFERTILIZED SOILS

Soil type or material	*Treatment*	*Total P, p.p.m.*	*Surface P, p.p.m.*	$\frac{\text{Surface } P}{\text{Total } P} \times 100$	*Residual*[a] $\frac{\text{Surface } P}{\text{Residual } P} \times 100$
Fort Collins loam	None	720	10.3	1.43	. . .
	Phosphated	764	23.3	3.06	30.2
Tripp fine sandy loam	None	380	11.1	2.92	. . . .
	Manure	470	39.4	8.40	31.4
Pryor silty clay loam	None	655	13.1	2.00	. . . .
	Manure	770	35.6	4.62	19.6
Sagemoor fine sandy loam	None	983	13.3	1.36	. . . .
	Manure	1,060	33.9	3.20	26.8
Rock phosphate		154,000	3,230	2.10	. . . .

[a] Percentage of residual P on the *surface* of particles. Residual P = difference between no treatment and phosphated or manure treatments.

Since the unfertilized soils all show less than 3 per cent of the total phosphorus on the surface of particles, the evidence clearly illustrates that the amount of surface phosphate arising from the residual phosphate is of a much higher order of magnitude than the native phosphate and that the residual phosphate is present in very finely divided particles. These data offer a logical explanation for the high residual value of the applied phosphate in these calcareous soils and show that, although precipitation reactions occur, the phosphate is held in extremely small crystals. Assuming that the residual phosphate is held in crystals similar to hydroxyapatite, with similar surface phosphate to

total phosphorus relationships with respect to surface area, the residual phosphate in the Fort Collins loam would have an area of 230 m.^{2} per gram, or an average particle size diameter of about 0.04 micron. Since neither the size distribution of the particles nor the exact nature of the residual phosphate is known, these figures represent comparative values only. These data illustrate, however, the importance and the need of soil studies concerning the nature of the physicochemical reactions occurring between the soil solution and the surface of the soil particles, and their relationship to the root membranes.

X. Extraction of Residual Phosphates by Various Chemicals

The nature of the residual phosphate in alkaline and calcareous soils has been studied also by attempts to fractionate the soil phosphorus with various extracting agents. Dean (1938) found that tricalcium phosphate and apatite were relatively insoluble in 0.25 *N* NaOH, whereas iron, aluminum, mono-, and dicalcium phosphates were soluble. The tricalcium phosphate and apatite were soluble in 0.5 *N* H_2SO_4. He showed that all the phosphate applied to the continuous plots at Rothamsted and Woburn was extracted by the combined alkali-acid extractions. In the slightly calcareous Rothamsted soil the bulk of the residual phosphate was acid-soluble, whereas in the acid Woburn sandy loam the major portion was alkali-soluble.

Williams (1950a) made extensive studies on methods for the fractionation of soil phosphorus, using a solution of 2.5 per cent acetic acid and 1 per cent 8-hydroxyquinoline solution, and 0.1 *N* NaOH. Williams (1950a) reversed the order of extraction used by Dean (1938) and obtained any dicalcium phosphate present in the acid extract. Recovery of added phosphate in contact with a soil for six weeks was practically complete for the combined extracts. The pH of this soil was varied by adding sulfur or $CaCO_3$. As the pH increased, the amount of residual phosphate extracted by acetic acid increased. These results confirm those of Dean (1938), and both authors concluded, reasoning by analogy from the solubilities of the known compounds, that the retention of phosphate in calcareous soils is due largely to precipitation by calcium.

Williams (1950b) also studied the residual phosphate in soils varying in pH from 6.5 to 8.9. The proportions of the residual phosphate extractable by acid increased as the pH increased. Although these methods of extraction do not make clean separations of the various forms of residual phosphate, they are valuable in indicating the main differences between calcareous soils and acid soils. By this method of fractionation apparently some of each form occur in both types of soils,

but the results do not show whether the composition of the acid soluble forms is the same in both alkaline and acid soils.

The correlation of phosphorus uptake by the plant and total phosphorus content in the plant with the total extractable phosphate was found by Williams (1950c) to be quite good for alkaline soils. The inorganic alkali-soluble fraction appeared to be the most suitable index of phosphorus fertility levels on the alkaline soils.

References

Abbott, G. A., and Bray, W. C. 1909. The ionization relations of ortho- and pyrophosphoric acid and their sodium salts. *J. Am. Chem. Soc.* **31**: 729–763.

Allison, L. E. 1943. The trend of phosphate adsorption by inorganic colloids from certain Indiana soils. *Soil Sci.* **55**: 333–342.

Arnon, D. I., Fratzke, W. E., and Johnson, C. M. 1942. Hydrogen ion concentration in relation to adsorption of inorganic nutrients by higher plants. *Plant Physiol.* **17**: 515–524.

Bassett, Jr., H. 1917. The phosphates of calcium. Part IV. The basic phosphates. *J. Chem. Soc.* **111**: 620–642.

Bates, R. G., and Acree, S. F. 1943. H values of certain phosphate chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60° C. *J. Research Natl. Bur. Standards* **30**: 129–155.

Benne, E. J., Perkins, A. T., and King, H. H. 1936. The effect of calcium ions and reaction upon the solubility of phosphorus. *Soil Sci.* **42**: 29–38.

Bjerrum, Niels. 1936. Investigations on the solubility of calcium phosphates. Paper read at the Nordic (19th Scandinavian) Scientist Meeting in Helsingfors August 11, 1936. Selected papers, edited by friends and co-workers. 1949. Copenhagen.

Boischot, P., Coppenet, M., and Hebert, J. 1950. The fixation of phosphoric acid on calcium carbonate in soils. *Plant and Soil* **2**: 311–322.

Brunauer, S., Emmett, P. H., and Teller, E. 1938. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.* **60**: 309–319.

Buehrer, T. F. 1932. The physico-chemical relationships of soil phosphates. *Arizona Agr. Expt. Sta. Tech. Bull.* **42**.

Burd, J. S. 1948. Chemistry of the phosphate ion in soil systems. *Soil Sci.* **65**: 227–248.

Davis, F. L. 1943. Retention of phosphate by soils: I. Effect of additions of iron and aluminum upon retention of phosphorus by virgin Hammond very fine sandy loam. *Soil Sci.* **56**: 457–478.

Dean, L. A. 1938. An attempted fractionation of the soil phosphorus. *J. Agr. Sci.* **28**: Pt. 2, 234–244.

Dundon, M. L., 1923. Surface energy of several salts. *J. Am. Chem. Soc.* **45**: 2658–2666.

Eisenberger, S., Lehrman, A., and Turner, W. D. 1940. The basic calcium phosphates and related systems. Some theoretical and practical aspects. *Chem. Revs.* **26**: 257–296.

Ensminger, L. E., and Larsen, H. W. E. 1944. Carbonic acid soluble phosphorus and lime content of Idaho soils in relation to crop response to phosphate fertilization. *Soil Sci.* **58**: 253–258.

ERICKSSON, S. 1940. Über die Einwirkung der Kalidüngung auf die Festlegung der Phosphorsäure in Boden. *Ann. Agr. Coll. Sweden* **8**: 87–130.

FARR, T. D. 1950. Phosphorus, properties of the element and some of its compounds. *TVA Chem. Eng. Rept.* **8**, Wilson Dam, Alabama.

FRIED, M., and DEAN, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

FULLER, W. H., and MCGEORGE, W. T. 1951. Phosphates in calcareous Arizona soils: II. Organic phosphorous content. *Soil Sci.* **71**: 45–50.

GAARDER, T. 1930. Die Bindung der Phosphorsäure im Erdboden. *Vestl. forstl. Forskssts. Middel.* **14**: 1–140.

GARDNER, R., and KELLEY, O. J. 1940. Relation of pH to phosphate solubility in Colorado soils. *Soil Sci.* **50**: 91–102.

GREAVES, J. E. 1910. The effect of soluble salts on insoluble phosphates. *J. Biol. Chem.* **7**: 287–319.

GREB, B. W. 1952. Organic phosphorus in calcareous Colorado soils. Master's thesis, Colorado Agricultural and Mechanical College, Fort Collins, Colorado.

GRUNER, J. W., and MCCONNELL, D. 1937. The problem of the carbonate-apatites. The structure of francolite. *Z. Krist.* **97**: 208–215.

HAZEMAN, J. F., BROWN, E. H., and WHITT, C. D. 1950. Some reactions of phosphate with clays and hydrous oxides of iron and aluminum. *Soil Sci.* **70**: 257–272.

HENDRICKS, S. B., and HILL, W. L. 1950. The nature of bone and phosphate rock. *Proc. Natl. Acad. Sci.* **36**: 731–737.

HIBBARD, P. L. 1931. Chemical methods for estimating the availability of soil phosphate. *Soil Sci.* **31**: 437–466.

HIBBARD, P. L. 1935. Factors influencing phosphate fixation in soils. *Soil Sci.* **39**: 337–358.

HOCKENSMITH, R. D., GARDNER, R., and GOODWIN, J. 1933. Comparison of methods for estimating available phosphorus in alkaline calcareous soils. *Colorado Agr. Expt. Sta. Tech. Bull.* **2**.

HODGE, H. C., LEFEVRE, M. L., and BALE, W. F. 1938. Chemical and X-ray diffraction studies of calcium phosphates. *Ind. Eng. Chem. Anal. Ed.* **10**: 156–161.

JACOB, K. D., HILL, W. L., ROSS, W. H., and RADER, JR., L. F. 1930. Composition of citrate-insoluble residues from superphosphates and ammoniated superphosphates. *Ind. Eng. Chem.* **22**: 1385–1392.

KARLSSON, N., and MATTSON, S. 1940. Electro-chemistry of soil formation: IV. The salt effect on amphoteric colloids and phosphate fixation. *Ann. Agr. Coll. Sweden* **8**: 406–424.

KOLTHOFF, I. M., and SANDELL, E. B. 1943. Textbook of Quantitative Inorganic Analysis, rev. ed. The Macmillan Co., New York.

KURTZ, T., DETURK, E. E., and BRAY, R. H. 1946. Phosphate adsorption by Illinois soils. *Soil Sci.* **61**: 111–125.

LEHR, J. J., and WESEMAEL, J. E. VAN. 1952. The influence of neutral salts on the solubility of soil phosphate, with special reference to the effect of the nitrates of sodium and calcium. *J. Soil Sci.* **3**: 125–135.

LEWIS, G. C., BAKER, G. O., and SNYDER, R. S. 1950. Phosphate fixation in calcareous soils. *Soil Sci.* **69**: 55–62.

LEWIS, G. N., and RANDALL, M. 1923. Thermodynamics, Chapter 28. McGraw-Hill Book Co., New York and London.

LOGAN, M. A., and TAYLOR, H. L. 1938. Solubility of bone salt. II. Factors affecting

its formation. III. Partial solution of bone and carbonate-containing calcium phosphate precipitates. *J. Biol. Chem.* **125**: 377–397.

LORAH, J. R., TARTAR, H. V., and WOOD, L. 1929. A basic phosphate of calcium and strontium and the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. *J. Am. Chem. Soc.* **51**: 1097–1106.

MACINTIRE, W. H., and SHAW, W. M. 1934. The transition of citrate soluble phosphate into citrate insoluble form in mixtures with limestones and with dolomite. *J. Am. Soc. Agron.* **26**: 656–661.

MATTSON, S., ERICKSSON, E., VAHTRAS, K., and WILLIAMS, E. 1940. Phosphate relationships of soil and plant: I. Membrane equilibrium and phosphate uptake. *Ann. Roy. Agr. Coll. Sweden* **16**: 457–484.

MATTSON, S., KOUTLER-ANDERSSON, E., MILLER, R. B., and VAHTRAS, K. 1951. Phosphate relationships of soil and plant: VIII. Electrokinetics, amphoteric behavior and solubility relationships of calcium phosphates. *Ann. Roy. Agr. Coll. Sweden* **18**: 128–153.

MAY, D. R., and KOLTHOFF, I. M. 1948. Studies on the aging of precipitates and coprecipitation. XL. The solubility of lead chromate as a function of particle size. *J. Phys. & Colloid Chem.* **52**: 836–854.

MCAULIFFE, C. D., HALL, N. S., DEAN, L. A., and HENDRICKS, S. B. 1947. Exchange reactions between phosphates and soils: Hydroxylic surfaces of soil minerals. *Soil Sci. Soc. Amer. Proc.* **12**: 119–123.

MCGEORGE, W. T. 1932. Electrodialysis as a measure of phosphate availability in soils and the relation of soil reaction and ionization of phosphates to phosphate assimilation. *Arizona Agr. Expt. Sta. Tech. Bull.* **38**.

MCGEORGE, W. T. 1939. Factors influencing the availability of native soil phosphate and phosphate fertilizers in Arizona soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **82**.

MCGEORGE, W. T. 1942. Studies on plant food availability in alkaline-calcareous soils: seedling tests and soil analysis. *Arizona Agr. Expt. Sta. Tech. Bull.* **94**.

MCGEORGE, W. T., and BREAZEALE, J. F. 1931a. Phosphate solubility studies on some unproductive calcareous soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **35**.

MCGEORGE, W. T., and BREAZEALE, J. F. 1931b. The relation of phosphate availability, soil permeability, and carbon dioxide to the fertility of calcareous soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **36**.

MCGEORGE, W. T., and BREAZEALE, J. F. 1932. Studies of iron, aluminum, and organic phosphates and phosphate fixation in calcareous soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **40**.

MURPHY, H. F. 1939. The role of kaolinite in phosphate fixation. *Hilgardia* **12**: 343–382.

NAFTEL, J. A. 1936. Soil liming investigations: II. The influence of lime on the sorption and distribution of phosphorus in aqueous and soil colloidal systems. *J. Am. Soc. Agron.* **28**: 740–752.

OLSEN, S. R., SCHMEHL, W. R., WATANABE, F. S., SCOTT, C. O., FULLER, W. H., JORDAN, J. V., and KUNKEL, R. 1950. Utilization of phosphorus by various crops as affected by source of material and placement. *Colorado Agr. Expt. Sta. Tech. Bull.* **42**.

OLSEN, S. R. 1952a. Measurement of surface phosphate on hydroxylapatite and phosphate rock with radiophosphorus. *J. Phys. Chem.* **56**: 630–632.

OLSEN, S. R. 1952b. The measurement of phosphorus on the surface of soil particles and its relationship to plant available phosphorus. Proceedings of a conference on

"The Use of Isotopes in Plant and Animal Research." Kansas State College, Manhattan, Kansas.

OVERSTREET, R., and DEAN, L. A. 1951. The availability of soil anions. *In* Mineral Nutrition of Plants, pp. 79–106. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

PAGE, J. B., and BODMAN, G. B. 1951. The effect of soil physical properties on nutrient availability. *In* Mineral Nutrition of Plants. pp. 133–166. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

PETERSON, H. B., and PASCHAL, J. L. 1951. A summary of phosphate fertilizer experiments in the fifteen Western States. *Research Rept.* 210, unpublished.

PRATT, P. F., and THORNE, D. W. 1948. Solubility and physiological availability of phosphate in sodium and calcium systems. *Soil Sci. Soc. Amer. Proc.* 13: 213–217.

RAVIKOVITCH, S. 1934. Anion exchange: I. Adsorption of the phosphoric acid ions by soils. *Soil Sci.* 38: 219–239.

REITEMEIER, R. F. 1946. Effect of moisture content on the dissolved and exchangeable ions of soils of arid regions. *Soil Sci.* 61: 195–214.

RUSSELL, E. W. 1950. Soil Conditions and Plant Growth, 8th ed. Longmans, Green and Co., London, New York, Toronto.

SCARSETH, G. D. 1935. The mechanism of phosphate retention by natural aluminosilicate colloids. *J. Am. Soc. Agron.* 27: 596–616.

SMITH, V. T. 1948. An evaluation of the carbon dioxide method of determining available phosphoric acid on high lime soils. *J. Am. Soc. Agron.* 40: 1045–1046.

STANBERRY, C. O. 1948. The behavior of phosphorus in an alkaline irrigated soil in Washington. *Soil Sci. Soc. Amer. Proc.* 13: 205–212.

STOUT, P. R., and OVERSTREET, R. 1950. Soil chemistry in relation to inorganic nutrition of plants. *Ann. Rev. Plant Physiol.* 1: 305–342.

TEAKLE, L. J. H. 1928. Phosphate in the soil solution as affected by reaction and cation concentrations. *Soil Sci.* 25: 143–161.

THORNE, D. W. 1946. Calcium carbonate and exchangeable sodium in relation to the growth and composition of plants. *Soil Sci. Soc. Amer. Proc.* 11: 397–401.

TOLMAN, B. 1950. Time and method of fertilizer application. *Am. Soc. Sugar Beet Technol. Proc.* 6: 422–427.

TOURKY, A. R., and EL WAKKAD, S.E.S. 1949. Solubility and particle size from a study on silver oxide. *J. Phys. & Colloid Chem.* 53: 1126–1134.

TRÖMEL, G., and MÖLLER, H. 1932. Die Bildung schwerlöslicher Calcium-phosphate aus wässriger Lösung und die Beziehungen zur Apatitgruppe. *Z. anorg. u. allgem. Chem.* 206: 227–240.

VOLK, G. W. 1945. Response to residual phosphorus of cotton in continuous culture. *J. Am. Soc. Agron.* 37: 330–340.

WADLEIGH, C. H., and RICHARDS, L. A. 1951. Soil moisture and the mineral nutrition of plants. Mineral Nutrition of Plants, pp. 411–450. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

WELCH, C. D., and NELSON, W. L. 1952. Fertility status of North Carolina soils as shown by soil tests. North Carolina Department of Agriculture, Raleigh, North Carolina.

WHITNEY, R. S., and GARDNER, R. 1942. The effect of carbon dioxide on soil reaction. *Soil Sci.* 55: 127–141.

WIKLANDER, L. 1950. Kinetics of phosphate exchange in soils. *Ann. Roy. Agr. Coll. Sweden* 17: 407–424.

WIKLANDER, L., HALLGREN, G., BRINK, N., and JONSSON, E. 1950. Studies on gyttja

soils. II. Some characteristics of two profiles from Northern Sweden. *Ann. Roy. Agr. Coll. Sweden* **17**: 24–36.

WILD, A. 1950. The retention of phosphate by soil. A review. *J. Soil Sci.* **1**: 221–238.

WILLIAMS, C. H. 1950a. Studies on soil phosphorus. I. A method for the partial fractionation of soil phosphorus. *J. Agr. Sci.* **40**: 233–242.

WILLIAMS, C. H. 1950b. Studies on soil phosphorus. II. The nature of native and residual phosphorus in some South Australian soils. *J. Agr. Sci.* **40**: 243–256.

WILLIAMS, C. H. 1950c. Studies on soil phosphorus. III. Phosphorus fractionation as a fertility index in South Australian soils. *J. Agr. Sci.* **40**: 257–262.

WILLIAMS, E. G. 1949. Phosphate fixation. *Natl. Agric. Advisory Service, Quart. Rev.* (Great Britain), 147–155.

WILLIAMS, E. G. 1950d. Phosphate fixation and availability. *J. Sci. Food Agri.* **8**: 244–248.

CHAPTER V

Organic Phosphorus in Soils

C. A. BLACK and C. A. I. GORING

The history of work on soil organic phosphorus dates back more than 100 years to the experiments of Mulder (1844), wherein he was unable to prepare phosphorus-free fractions of soil organic matter. The gradual accumulation of knowledge concerning the determination, amounts, forms, transformations, and importance of organic phosphorus in soils has in the past been traced in more or less detail by the reviews of Korolev (1910), Stewart (1910), Hudig and Domingo (1942), Kaila (1948), Pierre (1948), and Bremner (1951). These same subjects will be reviewed in the present paper, the purpose of which is to provide a more comprehensive summary than has recently been attempted, and at the same time to give an interpretation of the summarized results where that seems possible.

I. Determination

Ever since the beginning of work on soil organic phosphorus, there has been essentially only one general procedure in use for its determination, namely, determination of inorganic phosphorus in extracts before and after some treatment to change the organic phosphorus to inorganic form, the amount of organic phosphorus being obtained by difference. The treatment to change the organic phosphorus to the inorganic form may be applied to the soil itself or to an extract containing the organic phosphorus.

1. Differentiation of Organic and Inorganic Phosphorus

a. Selective Extraction. The first technique used to differentiate between organic and inorganic phosphorus was selective extraction. Ammonium hydroxide is an effective extractant for soil organic matter. Probably for this reason as well as the fact that he did not get a qualitative test for phosphate on ammoniacal extracts of soil, Grandeau (1872) inferred that the phosphorus present in the ammonia extract was all in organic form. This idea persisted for many years (R. Stewart, 1910; J.

Stewart, 1912; Dushechkin, 1929; Chirikov, 1939), although it was early challenged by Aso (1905) and discredited by Fraps (1911b).

Extraction of soil with mineral acid also was employed in the process of differentiating between organic and inorganic phosphorus (Eggertz and Nilson, 1889; Schmoeger, 1893; Vincent, 1917), on the assumption that soil inorganic phosphorus is acid-soluble and that soil organic phosphorus is acid-insoluble. More recent experience (Odynsky, 1936; Wrenshall and Dyer, 1939; Pearson, 1940; Ghani, 1944; Kheifets, 1948) shows that soil organic phosphorus displays appreciable solubility in acid, particularly where the strength is in excess of 1 or 2 normal.

b. Precipitation of Extracted Inorganic Phosphorus. The use of phosphate precipitants to separate organic and inorganic forms of phosphorus has not been entirely satisfactory. Grandeau (1872) obtained no precipitate at all, and others probably did not get complete precipitation. Schollenberger (1918) found that small amounts of inorganic phosphorus in ammonia extracts of soil would not respond to the magnesium ammonium phosphate test except in the presence of an additional quantity of inorganic phosphorus.

Another disturbing question in the precipitation of inorganic phosphorus with magnesia mixture and ammonium molybdate was the possible presence of organic phosphorus in the precipitates. Stewart (1912), Potter and Benton (1916), and Schollenberger (1918) were all concerned about the contamination of the magnesium ammonium phosphate precipitate with organic phosphorus. The work of Fingerling and Hecking (1911), Jegorow (1914), Seligson (1930), and Kursanov (1938) has demonstrated the difficulty of obtaining a precipitate free of organic phosphorus in the presence of phytin, an organic phosphorus compound found in soils.

c. Molybdenum Blue Colorimetric Method. Since 1927, most attempts to differentiate inorganic and organic phosphorus in soil extracts have been made with colorimetric methods. In that year, Parker and Fudge (1927) described the application of the Denigés and Fiske-Subbarrow methods to the determination of inorganic phosphorus in displaced soil solutions and water extracts containing organic phosphorus. Among the various forms of phosphorus, the colorimetric molybdenum blue method is specific to inorganic orthophosphate, and as far as is known it permits a clear differentiation of organic and inorganic phosphorus, provided that the former is not subject to hydrolysis and that the latter is present as soluble orthophosphate. In soil extracts, the amount of inorganic orthophosphate present is probably virtually identical with the total amount of inorganic phosphorus, although the presence of pyrophosphate and metaphosphate would bear investigation (Schmidt, 1951).

There is always some question, however, regarding the solubility of the inorganic phosphorus. Soil extracts may contain inorganic phosphorus in the form of suspended clay, and if some of this phosphorus becomes soluble in the acid solution used for developing the molybdenum blue color, it may either augment or diminish the apparent amount of organic phosphorus, according to the circumstances of the particular case.

The presence of a brown color in soil extracts, particularly alkali extracts, has long been a source of trouble in making accurate colorimetric determinations of inorganic phosphorus. Hockensmith, Gardner, and Goodwin (1933). Whitney and Gardner (1936), Dean (1938), Wrenshall and Dyer (1939), Pearson (1940), and Ghani (1942) have reported on various methods for eliminating the color, but the most satisfactory techniques appear to be the Dyer and Wrenshall (1938) procedure, in which the inorganic phosphorus is determined in the presence of the colored organic matter, and the isobutyl alcohol procedure (Berenblum and Chain, 1938; Pons and Guthrie, 1946; Martin and Doty, 1949), in which the molybdiphosphoric acid is selectively extracted from the colored aqueous phase.

2. *Quantitative Determination*

The various procedures proposed for determining organic phosphorus in soils can conveniently be classified into two categories according to the conditions under which the organic phosphorus is changed to the inorganic form. The first category includes those methods in which the organic phosphorus is changed to the inorganic form in the soil. It includes methods in which the organic phosphorus is changed to the inorganic form by high-temperature hydrolysis, wet combustion, and dry combustion. The second category includes methods in which the organic phosphorus is changed to the inorganic form after it has been extracted from the soil.

a. High-Temperature Hydrolysis. In attempting to demonstrate whether or not organic phosphorus was present in peat soils, Schmoeger (1893) extracted soils with 3.5 *N* hydrochloric acid before and after autoclaving the soils 10 to 20 hours at 130 to 160° C., and found that the amount of phosphorus extracted was approximately doubled by autoclaving. Similar results were obtained by Aso (1905) and Stewart (1910). Although high-temperature hydrolysis has not since been used with the objective of determining soil organic phosphorus, the evidence now available indicates that the technique is worthy of re-examination. Both Kossel (1881) and Amthor (1885) found that the major part of the phosphorus of nucleic acid was split off upon heating to a high temperature with water. Similar observations have been made with respect to

phytin (Jegorow, 1912; Jarosz, 1934; Fleury, 1945, 1946). Thompson (1948, unpublished data) found that dephosphorylation of phytin was complete when it was heated with water at 150° C. for a week, and Thompson and Black (1948) found that the same was true of soil organic phosphorus.

b. Dry Combustion. Two different types of dry combustion or ignition procedures have been proposed. The first type, proposed by Vincent (1937, 1938), depends on volatilization of the organic phosphorus. In Vincent's method, the soil is first extracted with 2.9 *N* hydrochloric acid. The acid-extracted soil is then ignited to volatilize the organic phosphorus. The ignited soil is extracted with concentrated nitric acid to remove the remaining inorganic phosphorus. The total phosphorus minus the phosphorus found in the two acid extracts is taken to represent organic phosphorus. Although no tests have been reported, it appears that results by this method may be low, owing to incomplete volatilization of organic phosphorus.

In the second type of procedure, inorganic phosphorus is determined in extracts of comparable ignited and nonignited samples of soil, the difference being taken as the amount of organic phosphorus present in the nonignited sample. Eggertz and Nilson (1889) were apparently the first to use such a procedure. They determined the phosphorus extracted from ignited peats with hot concentrated hydrochloric acid, subtracted the amount of phosphorus extracted from the nonignited samples with 0.55 *N* hydrochloric acid, and attributed the difference to organic phosphorus. Schmoeger (1893) and Vincent (1917) used similar methods. In all these methods, the effect of ignition was confounded with that of extraction, since the ignited samples were accorded a more rigorous extraction than the nonignited samples. This obvious defect was remedied by Stewart (1910), who used the same technique for both samples.

A second possible source of error was discovered by Fraps (1911a, 1911b) and Peterson (1911), who found that the dilute-acid solubility of certain naturally occurring iron and aluminum phosphates was increased by ignition. The presence of compounds of this type in soils would obviously have the effect of increasing the apparent amount of organic phosphorus. This possible source of error has been recognized by more recent investigators (Odynsky, 1936; Madanov, 1940; Ghani, 1944; Mattson, Williams, and Barkoff, 1950), but the methods used are probably incapable of making the same correction for inorganic phosphorus after ignition as before ignition in all soils.

A third source of error is incomplete extraction of the organic phosphorus mineralized by ignition. Russell and Prescott (1916) found that

some soils would adsorb phosphate from solutions of 0.2 *N* hydrochloric acid or 0.1 *N* citric acid. Thompson, Black, and Clark (1949) found that added inorganic phosphorus could not be recovered quantitatively from an acid subsoil by extraction with 1 *N* sulfuric acid. Several of the investigators cited above have used extractants no stronger than these.

In an attempt to reduce or eliminate possible errors from change in inorganic phosphorus solubility during ignition and incomplete extraction of mineralized organic phosphorus, Legg (1952, unpublished data) investigated the use of more concentrated acid. He found that soil samples could be warmed on the steam plate for 10 minutes with concentrated hydrochloric acid and then allowed to stand at room temperature for as long as 4 hours without appreciable hydrolysis of organic phosphorus. The concentrated acid extracted more inorganic phosphorus than did the weaker acids used previously, and the indicated amounts of organic phosphorus agreed fairly well with those obtained by an improved extraction method described in Section I.2.d(2).

c. Wet Combustion. In the wet combustion method for determining soil organic phosphorus, a sample of soil is treated with an oxidizing agent to decompose the organic matter and change the organic phosphorus to inorganic form. Comparable samples of unoxidized and oxidized soil are then treated with some extractant, and the increase in soluble inorganic phosphorus resulting from oxidation is taken to represent organic phosphorus. The oxidizing agent has usually been hydrogen peroxide, although Kurchatov (1936) used nitric and sulfuric acids and Salonen (1941) used potassium dichromate and sulfuric acid.

Karpinskiĭ and Zamyatina (1933) were the first to use hydrogen peroxide for changing the soil organic phosphorus to the inorganic form *in situ* as the basis for a quantitative determination of soil organic phosphorus. The hydrogen peroxide oxidation procedure has since been used, tested, or modified by a number of investigators, including Kurchatov and Pil (1935), van der Marel (1935), Kurchatov (1936), Dushechkin and Gorodisky (1936), Dickman and DeTurk (1938), Kaziev (1940), Pearson (1940), Sokolov (1940), Salonen (1941), Bertramson and Stephenson (1942), Ghani (1944), Bray and Kurtz (1945), Damsgaard-Sørenson (1946), Mehta (1951), and Legg (1952, unpublished data). As with the dry combustion method, the extractants have ordinarily been weak acids, and difficulty has been encountered with incomplete extraction of the mineralized phosphorus.

Dickman and DeTurk (1938) found that the apparent amounts of organic phosphorus increased with the quantity of 20 per cent hydrogen peroxide up to 10 ml. per gram of low organic matter soil and 15 ml. per gram of high organic matter soil. In general, however, quantity or

concentration of peroxide has not been given particular attention, probably because of the usual practice of adding it in increments until the reaction ceases.

Despite the general knowledge that treatment of soils with hydrogen peroxide does not oxidize all the organic carbon, and despite the existence of the paper of Jegorow (1912) reporting that the phosphorus of phytin was not completely mineralized by hydrogen peroxide, it has commonly been assumed that hydrogen peroxide completely mineralizes soil organic phosphorus. Mehta (1951) tested the completeness of mineralization by first treating samples of two soils by the hydrogen peroxide procedure of Bray and Kurtz (1945) and then extracting the same samples with hot sodium hydroxide. The sodium hydroxide extract contained a substantial amount of organic phosphorus, which showed that the peroxide treatment had left some residual organic phosphorus in the soil.

d. Extraction. In extraction procedures for quantitative determination of soil organic phosphorus, the soil is treated with one or more reagents designed to remove all the organic phosphorus without changing any of it to the inorganic form. Total and inorganic phosphorus are determined in aliquot portions of the extracts, and the difference is taken to represent organic phosphorus. The inorganic phosphorus present in the extracts is that brought out incidentally with the organic phosphorus and will include inorganic phosphorus derived from hydrolysis of organic phosphorus during extraction. In general, it does not represent the total inorganic phosphorus of the soil.

The Grandeau (1872) method may be considered the forerunner of present-day extraction methods. Grandeau's procedure consists in the following steps: (1) the soil is washed with dilute acid, and the excess acid is washed from the soil; (2) the soil is moistened with dilute ammonium hydroxide, and then washed with dilute ammonium hydroxide to remove organic matter; and (3) total phosphorus is determined in the ammonia extract.

The first step forward in principle was the revision of Grandeau's procedure in an attempt to correct for the inorganic phosphorus present in the ammonia extract. This work has already been mentioned in Section I.1. The next improvement was analysis of the acid extracts for organic phosphorus (Wrenshall and Dyer, 1939; Pearson, 1940). The remaining improvement has been in the extraction procedure; this research started with the work of Schollenberger (1918).

(1) Ammonium hydroxide extraction. Schollenberger (1918) investigated ammonium hydroxide as an extractant and obtained essentially maximum removal of phosphorus from the soil using a single

2-hour extraction with 1.1 *N* ammonium hydroxide at room temperature. Pearson (1940) made a more comprehensive study, and found that he obtained maximum removal of organic phosphorus by digesting 0.5 or 1 g. of soil for 18 hours at 90° C. with 400 ml. of 0.5 *N* ammonium hydroxide. Tests on three soils showed that this procedure removed about twice as much organic phosphorus as did the procedure of Schollenberger (1918). Both Schollenberger (1918) and Pearson (1940) used 0.1 *N* hydrochloric acid as preliminary extractant.

Wrenshall and Dyer (1939) proposed a procedure in which a 1 g. sample of soil was extracted first with 25 ml. of 4 *N* hydrochloric acid and second with 100 ml. of 2.9 *N* ammonium hydroxide, both extractions being made at room temperature. Legg (1952, unpublished data) found that, with seven soils, 20 per cent more organic phosphorus was extracted by the Wrenshall and Dyer (1939) method than by the Pearson (1940) method, indicating the superiority of the former method.

The work of Wrenshall and Dyer (1939) indicated that extraction of soils by their procedure removed almost all the soil phosphorus without causing any hydrolysis of organic phosphorus. Mehta (1951) found no evidence that hydrolysis occurred during extraction by their procedure, but Kheifets (1948) found that only about two-thirds of the total soil phosphorus was extracted by a procedure essentially the same as that of Wrenshall and Dyer (1939).

(*2*) *Sodium hydroxide extraction.* Schollenberger (1918) found that 0.25 *N* sodium, potassium, and lithium hydroxide extracted virtually the same amount of organic phosphorus as did 1.1 *N* ammonium hydroxide under the conditions described in Section I.2.d(1). Bower (1945), however, noted that hot 0.5 *N* sodium hydroxide extracted slightly more organic phosphorus from soils than did the ammonium hydroxide extraction procedure of Pearson (1940). Black, Pierre, and Allaway (1948) confirmed Bower's observation and found also that appreciable loss of organic phosphorus by hydrolysis took place during extraction. Ghani's (1943) results likewise indicated that organic phosphorus hydrolysis occurred during extraction with hot sodium hydroxide.

Because the foregoing results indicated the superiority of sodium hydroxide over ammonium hydroxide for extracting soil organic phosphorus, Mehta (1951) made a direct test to determine the efficacy of the Wrenshall and Dyer (1939) and the Pearson (1940) ammonium hydroxide extraction methods. He extracted samples of soils with hot sodium hydroxide after the samples had been pre-extracted according to the respective procedures and found that the sodium hydroxide extracts contained substantial quantities of organic phosphorus. Evidently,

neither of the two procedures had extracted all the organic phosphorus. Mehta (1951) made a similar test of Ghani's (1943) method of repeated room-temperature extraction with sodium hydroxide and again found that a subsequent extraction with hot sodium hydroxide removed an additional quantity of organic phosphorus. It appeared from these results that, although hot sodium hydroxide was unsatisfactory because of hydrolysis, it was nevertheless a better extractant than cold sodium hydroxide.

To determine whether the effectiveness of sodium hydroxide as an extractant could be utilized to advantage if two successive extractions of increasing severity were employed, Mehta (1951) subjected acid-leached samples of soil to successive extractions with sodium hydroxide at 90° C., or at room temperature and 90° C. More organic phosphorus was found with the successive cold and hot extractions than was found with the successive hot extractions. Practically no organic phosphorus was found in the second 90° C. extract. These results showed that it was possible to obtain a greater amount of organic phosphorus by combining a cold and hot extraction than by relying on a single hot extraction or repeated hot extractions. The organic phosphorus extracted at room temperature was found to be stable at room temperature but not at 90° C. The organic phosphorus in a second extract obtained at room temperature was stable for some time at 90° C. These results indicated that the organic phosphorus most easily extracted was also the most easily hydrolyzed.

Other experiments showed that the soil still contained organic phosphorus after extraction with sodium hydroxide at 90° C., but no appreciable quantity could be extracted by any of several techniques tried after the soil had been extracted at room temperature, 90° C., and 120° C. After a series of experiments in which hydrolysis and amount of organic phosphorus extracted were investigated as a function of concentration of sodium hydroxide and time and temperature of extraction, Mehta suggested that a practicable sodium hydroxide extraction procedure for use with 1 *N* hydrochloric acid-extracted soil was successive extraction of a 1 g. sample with 30 ml. of 0.5 *N* sodium hydroxide for 1 hour at room temperature, 60 ml. of 0.5 *N* sodium hydroxide for 8 hours at 90° C., and 30 ml. of 1 *N* sodium hydroxide for 2 hours at 120° C.

In a preliminary study of the hydrochloric acid pre-extraction procedures, Mehta (1951) found that increasing the concentration from 1 *N* to 4 *N* facilitated the subsequent extraction of organic phosphorus by sodium hydroxide and caused a small increase in the total quantity of organic phosphorus extracted. Legg (1952, unpublished data) found

that, with concentrated hydrochloric acid as pre-extractant, the extraction of organic phosphorus by sodium hydroxide was facilitated to the extent that the 120° C. extraction could be omitted. At the same time, the average amount of organic phosphorus extracted from seven soils was increased from 241 p.p.m. by Mehta's (1951) method to 258 p.p.m. by the modified procedure.

The Mehta-Legg procedure for organic phosphorus is probably more accurate than other recently proposed extraction and wet combustion methods, since by its use higher values for organic phosphorus are obtained. On the other hand, if higher values for organic phosphorus are obtained by wet or dry combustion methods than by the best extraction method available, it cannot at present be concluded with assurance that the results by the former methods are the more accurate. This is essentially the present state of affairs between the ignition method and the Mehta-Legg extraction method. As an average of results with seven soils, Legg found 258 p.p.m. of organic phosphorus by the extraction procedure described above and 285 p.p.m. of organic phosphorus by an improved dry combustion procedure employing concentrated hydrochloric acid as extractant. The higher results obtained by the dry combustion method may be the more accurate, but assurance that such is the case awaits the development of an extraction method that gives similar or greater amounts of organic phosphorus, or the use of new techniques not heretofore employed for testing the accuracy of soil organic phosphorus determinations.

II. Amounts

The amounts of organic phosphorus in soils may vary widely, as shown by the work of Schollenberger (1920), Dean (1938), Boratyński (1939), Weeks and Karraker (1941), Ghani and Aleem (1943b), Damsgaard-Sørensen (1946), Dmitrenko (1948), Garman (1948), Kaila (1948), Mattson, Williams, and Barkoff (1950), Mattson, Barkoff, and Williams (1950), Williams (1950a, 1950b), Fuller and McGeorge (1951a, 1951b), Godfrey (1951), Goring (1953b), Eid, Black, and Kempthorne (1953), and Thompson, Black, and Zoellner (1953), as well as by the various papers on methodology reviewed in Section I. The extreme values that have been reported in analyses of surface soils range from 18 p.p.m. of organic phosphorus in a sample of Orangeburg sandy loam from Mississippi (Pearson, 1940) to 1670 p.p.m. in a peat from Finland (Kaila, 1948). Expressed as a percentage of the total phosphorus, the values range from 2.6 to 75 per cent, both in samples from India (Basu and Kibe, 1945; Ghani and Aleem, 1943b). Work on the vertical distribution in soil profiles (Pearson and Simonson, 1940;

Kheifets, 1948; Mattson, Williams, and Barkoff, 1950; Mattson, Barkoff, and Williams, 1950; Fuller and McGeorge, 1951b; Godfrey, 1951) shows that the amount of organic phosphorus ordinarily decreases gradually with depth except in soils having pronounced horizon differentiation or in soils derived from recent sediments, where there may be irregularities. Although the surface horizon may contain in excess of 300 or 400 p.p.m. of organic phosphorus, the amount present at a depth of 3 feet is seldom in excess of 30 p.p.m.

In general, the amounts of organic phosphorus in soils are correlated positively with the amounts of organic carbon and nitrogen. It appears from the work of Schollenberger (1920), Dean (1938), Dickman and DeTurk (1938), Boratyński (1939), Pearson and Simonson (1940), Ghani and Aleem (1943b), Basu and Kibe (1945), Garman (1948), Kaila (1948), Kheifets (1948), Thompson and Black (1950), Williams (1950b), Fuller and McGeorge (1951a, 1951b), Godfrey (1951), Goring (1953b), and Thompson, Black, and Zoellner (1953), as well as from that of seven other investigations summarized by Dmitrenko (1948), that the organic matter of mineral soils contains carbon, nitrogen, and phosphorus in roughly the ratio 110:9:1 by weight. The ratio is wider in organic soils. In thirty Finnish peat soils, Kaila (1948) found about 700 parts of carbon and 30 parts of nitrogen to each part of organic phosphorus. From the work of Thompson, Black, and Zoellner (1953), it appears that the ratios of organic carbon and nitrogen to organic phosphorus increase with soil pH. Presumably, the rate of accumulation of organic phosphorus per unit of carbon and nitrogen is similar in acid and alkaline soils, but the resistance to mineralization is greater in acid soils than in alkaline soils. This point will be discussed further in Section IV.2.b.

III. Forms

In plants, animals, and microorganisms, which form the source material for soil organic phosphorus, there are five principal groups of organic phosphorus compounds, namely, phospholipids, nucleic acids, inositol phosphates, "metabolic" phosphates, and phosphoproteins. In investigations of the organic phosphorus compounds in soils, attention has been limited to the first three groups.

1. Phospholipids

Chemical evidence for the existence of phospholipids in soils is of two types. First, choline has been isolated from soil extracts by Aso (1905) and Shorey (1913). Choline is a product of the hydrolysis of lecithin, one of the phospholipids. Second, organic phosphorus has been

found in alcohol and ether extracts of soils by a number of investigators. Solubility in alcohol and ether is a property characteristic of the phospholipids.

Solubility in alcohol and ether has been used as the basis for a quantitative method as well as a qualitative test for phospholipids. The results of tests by Schmoeger (1893), Nannes (1899), Aso (1905), Korolev (1910), Drachev (1933), Kurchatov and Pil (1935), Vincent (1937), Wrenshall and McKibbin (1937), Pearson (1939), and Sokolov (1944, 1948) indicate that the amount of phospholipid phosphorus in soils is seldom in excess of 3 p.p.m. The highest values reported are those of Stoklasa (1911), who found 18, 22, and 34 p.p.m. in three different soils. Although it appears from these results that phospholipid phosphorus is usually present in only negligible quantities, final judgment must be withheld pending further investigation, because of the findings of Goring (1950) and Goring and Bartholomew (1950) that the extraction techniques used in obtaining these results were inadequate.

2. *Nucleic Acids*

Three different types of evidence have been advanced in support of the view that nucleic acid phosphorus is present in soils. The first type is based on identification of constituent parts of nucleic acid, the second on the relative susceptibility of nucleic acid and other organic phosphorus compounds to dephosphorylation, and the third on the differential solubility of nucleic acid and other organic phosphorus compounds.

Evidence of the first type has been obtained by Shorey (1911, 1912, 1913), Schreiner and Lathrop (1912), Bottomley (1919), Auten (1923), Wrenshall and McKibben (1937), and Wrenshall and Dyer (1941). Although not all investigators succeeded in identifying all constituents, the list of compounds identified in the hydrolyzate of preparations from soils includes phosphoric acid, pentose sugar, cytosine, adenine, guanine, uracil, hypoxanthine, and xanthine. The last two compounds are not primary hydrolytic products of nucleic acid but are derived from adenine and guanine. The results of these tests leave no doubt that constituent units of nucleic acids are present in soils and indicate that the units are present in part in combined form in soils. The evidence is not sufficient, however, to determine whether these compounds are present in soils largely as nucleic acids or as degradation products of nucleic acids, nor is it sufficient to establish that soil nucleic acids are closely similar to better known nucleic acids. The fact that purine constituents of soil nucleic acids are more resistant to acid hydrolysis than are purine constituents of plant and animal nucleic acids

(Wrenshall and Dyer, 1941) suggests that the nucleic acids from the different sources are not identical.

The early evidence (Schmoeger, 1893; Aso, 1905; Stewart, 1910) for the occurrence of nucleic acid in soils, based on experiments demonstrating the susceptibility of soil organic phosphorus to dephosphorylation in the presence of water at high temperatures, was inconclusive. As pointed out in Section I.2.a, organic phosphorus compounds other than nucleic acid may display this behavior. Subsequent experiments of Potter and Snyder (1918) on acid hydrolysis and of Wrenshall, Dyer, and Smith (1940) on alkaline hydrolysis showed that the rates of dephosphorylation of soil organic phosphorus preparations were slower than those of nucleic acid.

Bower (1949) obtained evidence of both the second and third types. He found that phytin and a mixture of lower phosphoric acid esters of inositol were precipitated almost quantitatively by calcium hydroxide, whereas yeast nucleic acid and guanine nucleotide remained soluble. He then separated the organic phosphorus of several soil extracts into two fractions by calcium hydroxide precipitation and tested the susceptibility of the soil fractions and authentic materials to dephosphorylation by hypobromite and two different enzyme systems. In each of the experiments conducted, the results verified the hypothesis that both nucleic acid and phytin were present in the soil preparations.

Because of the uncertainty connected with the nature of soil organic phosphorus, little work has been done on the quantitative determination of nucleic acid phosphorus in soils. Sokolov (1948) reported estimates of nucleic acid phosphorus in soils on the basis of two methods. In the first method, he determined total phosphorus in the precipitate resulting upon adding alcohol to a sodium hydroxide-sodium acetate extract of soil. In the second method, he determined purine nitrogen in the same precipitate and used an empirical factor to estimate phosphorus. Bower (1949) used the calcium hydroxide separation mentioned above on combined hydrochloric acid and sodium hydroxide extracts. The amounts of nucleic acid phosphorus obtained represented 38 to 58 per cent of the total organic phosphorus by Sokolov's (1948) first method, still higher percentages by his second method, and 17 to 33 per cent by Bower's (1949) method. There is as yet insufficient knowledge of nucleic acid phosphorus in soils to permit an evaluation of these results. The work of Adams (1952, unpublished data) to determine the quantities of the various nucleic acid fractions in soils, should provide an independent evaluation of results obtained by the Sokolov (1948) and Bower (1949) procedures and may, in addition, result in an improved method for determining nucleic acid phosphorus in soils.

3. *Inositol Phosphates*

Several types of evidence indicate the presence of inositol phosphates in soils. A number of investigators (Yoshida, 1940; Wrenshall and Dyer, 1941; Caldwell, 1951, unpublished data; Smith and Clark, 1951) have obtained chemical or microbiological evidence for the presence of inositol in the hydrolyzate of soil preparations. Inositol is the completely dephosphorylated nucleus of inositol hexaphosphoric acid, or phytic acid. Others have studied the resistance of soil preparations to dephosphorylation by enzymes and hypobromite. The tests of Bower (1949), mentioned in Section III.2, verified the existence of inositol hexaphosphoric acid, but those of Dyer, Wrenshall, and Smith (1940) and Wrenshall and Dyer (1941) with enzymes of the intestinal mucosa of the pig did not. Perhaps the major effort has been expended on determining ratios of iron to phosphorus or of inositol to phosphorus as a means of verification. Dyer, Wrenshall, and Smith (1940) and Wrenshall and Dyer (1941) found that the P:Fe ratio of their soil preparation agreed with that of ferric phytate obtained from authentic material in the same manner. Bower (1945) found that the inositol:P ratio of preparations from different soils agreed with the theoretical ratio for inositol hexaphosphoric acid, and in addition obtained evidence that another fraction contained inositol phosphoric acid esters having fewer than six phosphoric acid groups. Smith and Clark (1951) subjected some soil preparations to chromatographic analysis and verified the nature of the products by determining the inositol:P ratio and by failure of the soil products to separate from various added inositol phosphoric acid esters mixed therewith.

The first attempt to determine quantitatively the content of inositol phosphates in soils was apparently that of Vincent (1937), based on the erroneous assumption that phytin is soluble in alcohol. The techniques of Dyer, Wrenshall, and Smith (1940), Wrenshall and Dyer (1941), Bower (1945, 1949), and Jackman (1949) are all adaptable to quantitative work. Bower (1945) found that in three Iowa soils from 41 to 49 per cent of the organic phosphorus was present in the form of phytin and lower phosphoric acid esters of inositol and later (Bower, 1949) reported values of 67 to 83 per cent in the same soils. Jackman (1949) found by means of his modification of Bower's methods that from 30 to 149 p.p.m. of inositol phosphate phosphorus were present in a group of ten Iowa soils. The amount varied inversely with the pH. In the light of the findings of Smith and Clark (1951, 1952) regarding the impurity of inositol phosphate preparations obtained from soil by chemical fractionation, however, all available quantitative data on soil inositol phos-

phates are subject to question. The values reported above probably represent a considerable overestimate of the amounts actually present. Basing his method on the work of Jackman (1949) and Smith and Clark (1951, 1952), Caldwell (1951, unpublished data) developed a chromatographic method for inositol hexaphosphoric acid that gives quantitative results, but as yet no data are available on the content of this compound in soils.

IV. Transformations

1. Stabilization of Organic Phosphorus in Soils

If a soil profile contains as much as 2400 pounds of organic phosphorus per acre, as was found in some of Godfrey's (1951) work, it is obvious that many years must have been required for the accumulation, and hence that most of the organic phosphorus in the soil is not of recent origin. Since organic phosphorus compounds added to soils in the form of plant, animal, and microbial tissue are not particularly resistant to decomposition, there is evidently some condition peculiar to the status of organic phosphorus in soils that accounts for its stability.

Several hypotheses might be advanced to account for the failure of soil organic phosphorus to undergo rapid mineralization. First, it might be argued that the stability is caused by the presence of the organic phosphorus in viable tissue in the soil. The proportion of the organic phosphorus in viable tissue has never been evaluated, but Auten's (1923) estimates indicate that it is rather small. Second, it is possible that part of the soil organic phosphorus is different in nature from the major types of organic phosphorus compounds added to soils. Wrenshall and Dyer (1941) and Smith and Clark (1951) have obtained some evidence to support this view. The hypotheses that appear to account most credibly for the gross behavior, however, are first that soil organic phosphorus exists in an inherently unreactive state, and second that soils normally have a low level of enzyme activity.

The low concentration of organic phosphorus in displaced soil solutions and water extracts of soils is evidence for the existence of soil organic phosphorus in relatively inactive condition. Analyses of Pierre and Parker (1927), Kaila (1948), Fuller and McGeorge (1950, 1951a), and Yuen and Pollard (1951) indicate that the concentration is usually less than 1 p.p.m. Moreover, it appears from the work of Chouchak (1927) and Kaila (1948) that much of the "soluble" organic phosphorus may be present in microbial cells. The concentration of organic phosphorus attributable to solution processes is thus exceedingly low. This situation is in marked contrast to the appreciable solubility dis-

played by alkali salts of the abundant biological organic phosphorus compounds. The insolubility of the soil organic phosphorus probably results in part from the formation of insoluble salts with polyvalent cations (Umbreit, Burris, and Stauffer, 1949; Neuberg and Roberts, 1949; Jackman and Black, 1951; Wittcoff, 1951, p. 59) and in part from adsorption by clays or organic constituents (Smith, 1934; Gieseking, 1939; Hendricks, 1941; Speigel-Adolf, 1944; Astbury, 1947; Belozersky, 1947; Bower, 1949; Goring, 1950; Goring and Bartholomew, 1951, 1952; Wittcoff, 1951). Polar phosphate groups, basic amino groups, molecular forces, and hydrogen bonding are probably all involved in the interactions between organic phosphorus compounds and soil (Hendricks, 1941; Bradley, 1945; Goring and Bartholomew, 1952).

In a series of experiments on decomposition of organic matter in soils, it has been found by Broadbent and Norman (1947), Broadbent (1948), and Hallam (1952) that soil organic carbon and nitrogen are mineralized at a more rapid rate in the presence than in the absence of added decomposable organic substances. They have concluded that one reason for the resistance of soil organic matter to decomposition is the normally low level of microbiological activity, i.e., enzyme activity, in the soil.

Tests of the various hypotheses to account for the persistence of soil organic phosphorus as a whole have not yet been conducted, but some work has been done on phytin, where the choice of hypotheses is fairly clearly between insolubility and enzyme activity. The experiments of Jackman and Black (1952a, 1952b) demonstrated the presence of phytase activity in soils, and indicated that insolubilty of soil phytin was of far greater importance than the level of phytase activity in limiting the rate of hydrolysis of the soil phytate phosphorus. In an additional experiment, Jackman (1949) found that maintaining soil phytase activity at an artificially high level for 15 weeks by periodic additions of carbohydrates and nitrogen resulted in a perceptible decrease in content of inositol phosphate phosphorus in six soils. These results indicate that the level of enzyme activity does have a measurable effect. Further verification of the results of the latter experiment is needed, however, because it is now known that the method of analysis employed includes some soil organic phosphorus not present as inositol phosphates.

2. Mineralization

a. Evidence. Two types of evidence indicate that soil organic phosphorus undergoes mineralization. The first is based on changes in soils as a result of long-continued treatment. Several investigators (Scholl-

enberger, 1920; Pearson, 1940, unpublished data; Garman, 1948; Thompson and Black, 1950; Thompson, Black, and Zoellner, 1953) have found that, in comparable samples of virgin and cultivated soils, the content of organic phosphorus is usually the lower in cultivated soils. DeTurk (1938) and Korableva (1951) found that the organic phosphorus content of cultivated soil decreased with time. Khvorov and Onokhava (1939) found that when virgin soils were brought under cultivation the content of organic matter decreased; the content of citric acid-soluble phosphorus increased for the first few years of cultivation, and then gradually decreased. Damsgaard-Sørensen (1946) and Kaila (1948) found that limed soils contained less organic phosphorus than did the soil of corresponding acid, unlimed plots. These results can all be explained on the basis of organic phosphorus mineralization; in themselves, however, they do not constitute sufficient evidence.

The second type of evidence is based on laboratory experiments conducted over a relatively short period of time. Robinson (1937) found that the amount of inorganic phosphorus removed by Truog's dilute sulfuric acid-ammonium sulfate extractant increased in air-dry soil samples during a year's storage. The increase in extractable inorganic phosphorus was correlated positively with the amount of total nitrogen in the soils. Ghani and Aleem (1943a) found that during a 10-week incubation the content of soil organic phosphorus decreased. At the same time, the content of acetic acid-soluble inorganic phosphorus increased, although not to the same extent. Salonen (1946) found that, although organic phosphorus soluble in 0.25 *N* sodium hydroxide usually decreased during incubation, the inorganic phosphorus soluble in the same extractant usually decreased also. It was subsequently found for a large number of soils by Thompson (1947), Kaila (1948), Bower (1949), and Thompson, Black, and Zoellner (1953) that the increase in extractable inorganic phosphorus produced during incubation agreed closely with the decrease in organic phosphorus, thus demonstrating more conclusively that soil organic phosphorus may undergo mineralization. These investigators used strong mineral acid or consecutive strong mineral acid-ammonium hydroxide extraction.

b. Association with Other Soil Properties. The work of Thompson and Black (1950) and Thompson, Black, and Zoellner (1953) showed that both the quantity of organic phosphorus and the rate of organic phosphorus mineralization in a group of soils were correlated positively with the amounts of organic carbon and nitrogen in soils. The rate of organic phosphorus mineralization was correlated positively with the rates of organic carbon and nitrogen mineralization. Moreover, the amounts of organic phosphorus, nitrogen, and carbon mineralized cor-

responded roughly to the proportions in which the respective constituents occurred in the soil organic matter. These results indicate that the behavior of organic phosphorus is correlated with the behavior of the organic matter as a whole.

On closer examination, it appears that the behavior of organic phosphorus is not entirely analogous to that of organic carbon and nitrogen. The work of Ghani and Aleem (1943a), Damsgaard-Sørensen (1946), and Kaila (1948), showing a decrease in total organic phosphorus upon liming acid soils, indicates that the rate of organic phosphorus mineralization increases with the pH. Although similar observations have often been made with respect to nitrogen mineralization, Thompson, Black, and Zoellner (1953) found with fifty unlimed soils that mineralization of organic phosphorus increased markedly with pH but that mineralization of organic carbon and nitrogen did not. The existence of these same pH effects on mineralization in the field is indicated by the fact that the ratios of total organic carbon and total nitrogen to total organic phosphorus increased with soil pH in the same samples.

c. Effect of Soil Conditions. The rate of organic phosphorus mineralization may vary appreciably during the year because of the continual changes of microbial activity in response to variations in soil conditions. The work of Thompson and Black (1948), Bower (1949), and Thompson (1950) indicates that mineralization increases with temperature, particularly above about 25 or 30° C. Fehér, Frank, and Manninger (1939) found that citric acid-soluble phosphorus in soils was greater after incubation at 50 to 75 per cent of the water-holding capacity than at either 25 or 90 per cent of the water-holding capacity. In contrast, Fehér (1934) and Fehér and Frank (1936a) found that the content of citric acid-soluble phosphorus in forest soils throughout the year was correlated negatively with the product of soil water percentage and soil temperature in the field at the time of sampling. Fehér and coworkers (Fehér, 1934, 1935; Fehér and Frank, 1936a, 1936b; Fehér, Frank, and Manninger, 1939) have correlated citric acid-soluble phosphorus with numbers of soil microorganisms, but from the inconsistency in results between experiments the relationships appear to be complex.

There is some evidence that organic phosphorus mineralization may be affected by previous heating, drying, or freezing of the soil. These treatments have been reported by many investigators to increase the solubility of soil organic matter. DeLong, Sutherland, and Archer (1940) found that previous heating increased the amounts of both organic and inorganic phosphorus extracted from soils by Truog's dilute sulfuric acid-ammonium sulfate extractant. Drying increased the

amount of inorganic phosphorus extracted but had no consistent effect on organic phosphorus. Thompson's (1947) finding that appreciable organic phosphorus mineralization appeared to occur for only about a week after air-dried soils had been moistened may have resulted from an effect of drying on susceptibility of a part of the organic phosphorus to mineralization. Yuen and Pollard (1951) found that the content of organic phosphorus in the soil solution was highest in the spring and lowest in the autumn, which likewise suggests an effect of winter freezing on susceptibility of a part of the organic phosphorus to mineralization.

d. Added Organic Materials. When organic material free of inorganic phosphorus is allowed to undergo partial decomposition in soils, the net effect on the quantity of inorganic phosphorus depends to some extent on the organic phosphorus percentage in the added material. Mineralization will result with such substances as nucleic acid and the simple carbohydrate phosphates, which contain high percentages of organic phosphorus (Scharrer and Keller, 1940; Dyer and Wrenshall, 1941; Pearson, Norman, and Ho, 1941; Pinck, Sherman, and Allison, 1941); and at the other extreme, immobilization will result with such substances as dried blood and carbohydrates, which contain little or no organic phosphorus (Chouchak, 1929; Taylor, 1946; Kaila, 1948; Fuller and McGeorge, 1950).

The situation of greatest practical significance lies between the two extremes of high and low organic phosphorus. Lockett (1938), Chang (1939, 1940), Mamchenko (1941), Pearson, Norman, and Ho (1941), Shrikhande (1948), and Kaila (1948, 1949a, 1949b) have contributed to an understanding of this problem. A tabulation of data obtained by these investigators shows that where various organic materials were decomposed for periods of a month or less by a mixed flora, initial mineralization of organic phosphorus occurred where the material contained 0.15 to 0.78 per cent organic phosphorus, and initial immobilization occurred where it contained 0 to 0.21 per cent organic phosphorus. Assuming a carbon content of 45 per cent in the original organic materials, the data indicate that initial mineralization will occur if the C:organic P ratio is below about 200, and that initial immobilization will occur if the ratio is above about 300. Interpretation of these results in terms of the type of organic substances commonly added to soils indicates that immobilization of phosphorus should be a normal occurrence with such substances as straws and green manures, and that mineralization should usually result with animal manures. Before these results can be interpreted in terms of availability of the phosphorus to plants, however, at least two additional factors should be considered.

In the first place, the organic substances commonly added to soils contain, on the average, about as much inorganic phosphorus as organic phosphorus. If immobilization occurs, the microorganisms can, in effect, draw on the inorganic phosphorus in the decomposing materials. Since in the majority of recorded instances less than half the inorganic phosphorus was immobilized as organic phosphorus, a substantial part of the total phosphorus would still be in inorganic form. The significance of this remaining inorganic phosphorus to plants, however, can not yet be determined from the chemical evidence, because the latter does not distinguish between microbial and nonmicrobial inorganic phosphorus. Whether it is organic or inorganic, the phosphorus in microbial tissue is probably "immobilized" as far as the plant is concerned.

In the second place, the critical range of the C:organic P ratio that determines whether mineralization or immobilization predominates may be wider in practice than in the laboratory experiments. The usual practice of adding nitrogen to low-nitrogen materials in laboratory experiments should lower the critical C:organic P ratio in a particular material; in a group of materials, where there is normally a correlation between nitrogen and organic phosphorus, it should narrow the critical range of the C:organic P ratio. This hypothesis receives some support from the work of Fuller and Rogers (1951), but further tests are necessary.

The foregoing interpretation of the biochemical evidence on short-term availability of organic phosphorus in organic materials gives a rather more gloomy picture than the evidence from plant growth experiments reviewed in Chapter VIII. There may be several reasons for the difference, pointed out therein. To avoid placing undue emphasis on short-term effects, however, it should be recalled that under practical conditions a crop may occupy the land from several months to a year or more after the application of organic materials. Moreover, the total effect of organic materials on the phosphorus supply involves not only the contribution of the most recent addition, but also the unexhausted residual effects of previous additions. The data of Damsgaard-Sørensen (1946) and Korableva (1951) obtained from field experiments with manure indicate that the added organic phosphorus is largely mineralized, with the result that the content of soil inorganic phosphorus is increased.

V. Importance

Numerous experiments have demonstrated the greater or lesser availability to plants of the phosphorus added in organic form to culture solutions, sand cultures, or soils, but relatively few experiments have

been conducted on soil organic phosphorus in its natural state. The first experiment of the latter type appears to be that of Vincent (1937), in which it was found that during growth of crops there was a reduction in amounts of both inorganic and organic soil phosphorus soluble in 2 per cent citric acid.

Chirikov and Volkova (1941) separated the total soil phosphorus into five fractions on the basis of solubility in chemical extractants, and then classified the various fractions in order of decreasing availability on the basis of plant growth tests. The sodium hydroxide-soluble fraction, containing most of the organic phosphorus together with some inorganic phosphorus, was classified in the fourth category. It appeared to be of no value. Williams (1950c) conducted a similar experiment with five soils, in which removal of 7.5 p.p.m. of phosphorus from the soil by a wheat crop was accompanied by a reduction of 8.1 p.p.m. in soil phosphorus extracted in three fractions, distributed as follows: 4.5 p.p.m. in the acetic acid-soluble inorganic fraction, 2.5 p.p.m. in the alkali-soluble inorganic fraction, and 1.0 p.p.m. in the organic fraction. In other experiments, he found that the phosphorus in the soil fractions was correlated significantly with the phosphorus percentage in wheat plants in the case of the acetic acid-soluble and alkali-soluble inorganic fractions, but not in the case of the organic fraction. These results of Chirikov and Volkova (1941) and Williams (1950c) indicate that availability of soil phosphorus to plants is primarily a matter of the inorganic phosphorus status, and that organic phosphorus is of little or no importance.

Eid, Black, and Kempthorne (1951, 1953) conducted three experiments in which phosphorus availability, estimated in a group of soils by plant growth, was related by multiple regression to the following four soil phosphorus fractions: (1) "available" inorganic phosphorus found by the dilute ammonium fluoride-hydrochloric acid extractant of Bray and Kurtz (1945); (2) organic phosphorus soluble in 1 per cent potassium carbonate and dephosphorylated by hypobromite; (3) organic phosphorus soluble in 1 per cent potassium carbonate and not dephosphorylated by hypobromite; and (4) organic phosphorus not extracted by potassium carbonate but extracted by the Pearson (1940) method for total organic phosphorus. Organic phosphorus fractions 3 and 4 were of no significant independent value in predicting plant-available phosphorus in any of the experiments. In two of the experiments, the plants were grown at soil temperatures of 20 and 35° C. At 20° C., organic fraction 2 likewise was of no significant value in predicting plant-available phosphorus independent of inorganic fraction 1. At that temperature, plant-available phosphorus depended almost entirely on inorganic

fraction 1. At 35° C., however, organic fraction 2 was of significant value in predicting plant-available phosphorus independent of inorganic fraction 1, but inorganic fraction 1 was not of significant value independent of organic fraction 2. The third experiment was conducted in the same general way as the first two, except that the soils were incubated in a moist condition at different temperatures before the growth of the plants, and during growth the soil temperature was allowed to fluctuate with that of the greenhouse. In this experiment, the various pretreatments had no significant effect on plant-available phosphorus. Organic fraction 2 was of significant independent value in predicting plant-available phosphorus, but inorganic fraction 1 was not.

The results of all three experiments served to verify the hypothesis that soil organic phosphorus may be of significance in the phosphorus nutrition of the crop. It was postulated from the results of the first two experiments that soil organic phosphorus *per se* is of little or no value in the phosphorus nutrition of plants, and that it becomes of value when it is changed to the inorganic form. Since mineralization of organic phosphorus proceeds several times faster at 35° C. than at 20° C., the results might be attributed to the availability of much more mineralized organic phosphorus at high soil temperatures than at low soil temperatures. In addition, the results of the third experiment suggest that the plant must be present while mineralization is occurring to take advantage of the extra source of phosphorus; otherwise, the special value of the mineralized phosphorus is lost by equilibration with the inorganic phosphorus of the soil.

Although there is as yet no evidence to disprove the correctness of the mechanism suggested, it must nevertheless be recognized that the existing evidence has not established the sufficiency of this mechanism to account for the observed results. Whether or not the suggested mechanism is correct, however, the experiments demonstrated that knowledge of the quantity of an appropriate organic phosphorus fraction made possible a more precise prediction of soil phosphorus availability than was the case with information on only inorganic phosphorus availability.

Clark (1952) conducted an experiment in which it was found that plant-available phosphorus measured at 20° C. did not depend to a significant extent on either the total organic phosphorus or the organic phosphorus soluble in potassium carbonate and dephosphorylated by hypobromite. Instead, it depended on a fraction of soil inorganic phosphorus.

Goring (1953a) developed a modification of the isotope dilution technique of Fried and Dean (1952) by which he could determine the

amount of soil phosphorus available to soil microorganisms. Using this technique, Goring and Zoellner (1953) found that the soil phosphorus available to microorganisms depended on both the inorganic phosphorus extracted by the Bray and Kurtz (1945) method and the net amount of organic phosphorus synthesized by the microorganisms. The latter was presumed to be correlated with the amount of organic phosphorus mineralized, and to derive its significance from this correlation. In the same soils, however, the amount of soil phosphorus available to plants according to the Fried and Dean (1952) method depended on the inorganic phosphorus extracted by the Bray and Kurtz (1945) method, but not on the net amount of organic phosphorus synthesized by microorganisms. If the assumption is correct that net synthesis was correlated with the amount of organic phosphorus mineralized, these data indicate that organic phosphorus mineralization was not of significant value, independent of correlation with the extracted inorganic phosphorus, in determining the amount of soil phosphorus available to plants.

Of all the experiments that have been conducted, only those of Vincent (1937) and Eid, Black, and Kempthorne (1951, 1953) indicate that soil organic phosphorus may be of significance in the phosphorus nutrition of plants. The negative results of Clark (1952) can be accounted for on the basis of technique, since his experimental conditions were those under which Eid, Black, and Kempthorne (1951, 1953) found no significant value of soil organic phosphorus. The data of Goring and Zoellner (1953) cannot be accounted for in this way, since the greenhouse experiment from which the plant data were obtained was conducted under conditions found by Eid, Black, and Kempthorne (1951, 1953) to favor the importance of organic phosphorus. Whether the same can be said of the experiments of Chirikov and Volkova (1941) and Williams (1950c) is not known. Further research is needed on this important problem.

References

Amthor, C. 1855. Ueber das Nuclein der Weinkerne. Reifestudien an Weinkernen. *Z. Physiol. Chem.* **9**: 138–144.

Aso, K. 1905. On organic compounds of phosphoric acid in the soil. *Coll. Agr., Tokyo Imp. Univ., Bull.* **6**: 277–284.

Astbury, W. T. 1947. X-ray studies of nucleic acids. *Symposia Soc. Exptl. Biol.* **1**: 66–76.

Auten, J. T. 1923. Organic phosphorus of soils. *Soil Sci.* **16**: 281–294.

Basu, J. K., and Kibe, M. M. 1945. The fertility of a typical black cotton soil as related to its different phosphorus fractions, after ten years of manuring. *J. Univ. Bombay* **14**, P. 3A: 29–34.

Belozersky, A. N. 1947. On the nucleoproteins and polynucleotides of certain bacteria. *Cold Spring Harbor Symposia Quant. Biol.* **12**: 1–6.

BERENBLUM, I., and CHAIN, E. 1938. An improved method for the colorimetric determination of phosphate. *Biochem. J.* **32**: 295–298.

BERTRAMSON, B. R., and STEPHENSON, R. E. 1942. Comparative efficiency of organic phosphorus and of superphosphate in the nutrition of plants. *Soil Sci.* **53**: 215–227.

BLACK, C. A., PIERRE, W. H., and ALLAWAY, W. H. 1948. Forms of phosphorus in soils and their availability to plants. *Iowa Agr. Expt. Sta. Ann. Rept.* 1948, pp. 101–104.

BOGATYŃSKI, K. 1939. Zawartość fosforu organicznego w niektórych glebach polskich. *Roczniki Nauk Rolniczych i Leśnych* **48**: 77–90.

BOTTOMLEY, W. B. 1919. The isolation from peat of certain nucleic acid derivatives. *Proc. Roy. Soc. (London)* **90B**: 39–44.

BOWER, C. A. 1945. Separation and identification of phytin and its derivatives from soils. *Soil Sci.* **59**: 277–285.

BOWER, C. A. 1949. Studies on the forms and availability of soil organic phosphorus. *Iowa Agr. Expt. Sta. Research Bull.* **362**.

BRADLEY, W. F. 1945. Molecular associations betwen montmorillonite and some polyfunctional organic liquids. *J. Am. Chem. Soc.* **67**: 975–981.

BRAY, R. H., and KURTZ, L. T. 1945. Determination of total, organic, and available forms of phosphorus in soils. *Soil Sci.* **59**: 39–45.

BREMNER, J. M. 1951. A review of recent work on soil organic matter. Part I. *J. Soil Sci.* **2**: 67–82.

BROADBENT, F. E. 1948. Nitrogen release and carbon loss from soil organic matter during decomposition of added plant residues. *Soil Sci. Soc. Am. Proc.* (*1947*) **12**: 246–249.

BROADBENT, F. E., and NORMAN, A. G. 1947. Some factors affecting the availability of the organic nitrogen in soil—a preliminary report. *Soil Sci. Soc. Am. Proc.* (*1946*) **11**: 264–267.

CHIANG, S. C. 1939. The transformation of phosphorus during the decomposition of plant materials. *Soil Sci.* **48**: 85–99.

CHIANG, S. C. 1940. Assimilation of phosphorus by a mixed soil population and by pure cultures of fungi. *Soil Sci.* **49**: 197–210.

CHIRIKOV, F. V. 1939. (A method for determining forms of phosphate in soils.) *Khimizatsiya Sotsialist. Zemledeliya 1939*, No. 10–11: 59–63.

CHIRIKOV, F. V., and VOLKOVA, V. V. 1941. (The availability to plants of the phosphoric acid of different forms of soil phosphate.) *Vestnik Udob. Agrotekh. Agropochvoved.* **3**: 115–133 [*Soils and Fertilizers* **8**: 78–79 (1945)].

CHOUCHAK, D. 1927. Sur l'antagonisme entre les plantes cultivées et les bactéries du sol dans leur nutrition minérale. *Compt. rend.* **185**: 82–85.

CHOUCHAK, M. 1929. La lutte entre les plantes cultivées et les microorganismes du sol pour leur nutrition minérale; action du sang desséché sur l'engrais phosphaté. *Compt. rend.* **189**: 262–264.

CLARK, R. E. 1952. Utilization of soil organic phosphorus by plants. Ph.D. thesis, Cornell University, Ithaca, New York.

DAMSGAARD-SØRENSEN, P. 1946. Studier over Jordens Fosforsyreindhold. IV. Det organisk bundne Fosfor. *Tidsskr. Planteavl* **50**: 653–675.

DEAN, L. A. 1938. An attempted fractionation of the soil phosphorus. *J. Agr. Sci.* **28**: 234–246.

DELONG, W. A., SUTHERLAND, A. J., and ARCHER, P. L. 1940. Observations on the

easily-soluble phosphorus in a soil of the Appalachian upland podsolized type. *Sci. Agr.* **21**: 92–102.

DeTurk, E. E. 1938. Changes in the soil of the Morrow plots which have accompanied long-continued cropping. *Soil Sci. Soc. Amer. Proc.* **3**: 83–85.

Dickman, S. R., and DeTurk, E. E. 1938. A method for the determination of the organic phosphorus of soils. *Soil Sci.* **45**: 29–39.

Dmitrenko, P. A. 1948. (The phosphorus content in the organic portion of the soil.) *Pochvovedenie* **1948**: 495–501.

Drachev, S. M. 1933. (The effect of tillage and fertilizers on the phosphates in podzolic soils.) Pochvovedenie **28**: 240–251.

Dushechkin, A. I. 1929. (The forms of phosphorus in the soil and the response of soils to phosphate fertilizers.) *Udobrenie i Urozhai* **4**: 195–201.

Dushechkin, A. I., and Gorodisky, V. I. 1936. (The effect of H_2O_2 on soil, as a method of separating the organic and mineral forms of P.) *Trudy Inst. Agrogrunt. Khem.* **1**: 4–14 [*Bibl. Soil Sci.* **1934–1937**: 70 (1938)].

Dyer, W. J., and Wrenshall, C. L. 1938. An improved method for the determination of phosphate by photoelectric colorimetry. *Canadian J. Research* **16B**: 97–108.

Dyer, W. J., and Wrenshall, C. L. 1941. Organic phosphorus in soils: III. The decomposition of some organic phosphorus compounds in soil cultures. *Soil Sci.* **51**: 323–329.

Dyer, W. J., Wrenshall, C. L., and Smith, G. R. 1940. The isolation of phytin from soil. *Science* **91**: 319–320.

Eggertz, C. G., and Nilson, L. F. 1889. Chemische Untersuchung von Moor- und Torfböden. *Biedermanns Cent.* **18**: 664–668.

Eid, M. T., Black, C. A., and Kempthorne, O. 1951. Importance of soil organic and inorganic phosphorus to plant growth at low and high soil temperatures. *Soil Sci.* **71**: 361–370.

Eid, M. T., Black, C. A., and Kempthorne, O. 1953. Significance of soil organic phosphorus to plant growth. *Iowa Agr. Expt. Sta. Research Bull.* (In Press.)

Fehér, D. 1934. Untersuchungen über den periodischen Kreislauf des Phosphors in den Waldböden. *Phosphorsäure* **4**: 508–529.

Fehér, D. 1935. Beiträge zum Problem des mikrobiologischen Kreislaufes des Phosphors in Boden. *Phosphorsäure* **5**: 706–713.

Fehér, D., and Frank, M. 1936a. Untersuchungen uber den periodischen Kreislauf des Stickstoffes, des Phosphors und des Kaliums in den Waldböden. *Z. Pflanzenernähr. Düng. Bodenk.* **43**: 5–33.

Fehér, D., and Frank, M. 1936b. Mikrobiologische Untersuchungen über den dynamischen Kreislauf des Stickstoffs, des Phosphors und des Kaliums in den Ackerböden. *Bodenkunde u. Pflanzenernähr.* **1**: 196–219.

Fehér, D., Frank, M., and Manninger, G. A., Jr. 1939. Experimentelle Untersuchungen über den Einfluss der Mikroorganismentätigkeit auf das dynamische Verhalten der leichtlöslichen Phosphor-, Kali- und Stickstoffverbindungen des Bodens. *Bodenkunde u. Pflanzenernähr.* **13**: 341–352.

Fingerling, G., and Hecking, A. 1911. Zur Frage der quantitativen Trennung der organischen Phosphorverbindungen von den Phosphaten in Futtermitteln. *Biochem. Z.* **37**: 452–456.

Fleury, P. 1945. Sur l'hydrolyse chimique de l'acide inositohexaphosphorique. *Compt. rend.* **221**: 416–418.

FLEURY, P. 1946. Etude de l'hydrolyse chimique de l'acide inositohexaphosphorique. *Bull. soc. chim. biol.* **28**: 282–286.

FRAPS, G. S. 1911a. Effect of ignition on the solubility of soil phosphates. *J. Ind. Eng. Chem.* **3**: 335.

FRAPS, G. S. 1911b. Organic phosphoric acid of the soil. *Texas Agr. Exp. Sta. Tech. Bull.* **136**.

FRIED, M., and DEAN, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

FULLER, W. H., and MCGEORGE, W. T. 1950. Phosphates in calcareous Arizona soils: I. Solubilities of native phosphates and fixation of added phosphates. *Soil Sci.* **70**: 441–460.

FULLER, W. H., and MCGEORGE, W. T. 1951a. Phosphates in calcareous Arizona soils: II. Organic phosphorus content. *Soil Sci.* **71**: 45–49.

FULLER, W. H., and MCGEORGE, W. T. 1951b. Phosphates in calcareous Arizona soils: III. Distribution in some representative profiles. *Soil Sci.* **71**: 315–323.

FULLER, W. H., and ROGERS, R. N. 1951. Utilization of phosphorus from barley residues in calcareous soils. *Arizona Agr. Expt. Sta. Tech Bull.* **123**.

GARMAN, W. L. 1948. Organic phosphorus in Oklahoma soils. *Proc. Oklahoma Acad. Sci. (1947)* **28**: 89–100.

GHANI, M. O. 1942. Determination of organic phosphorus in alkali extracts of soils. *Indian J. Agr. Sci.* **12**: 336–340.

GHANI, M. O. 1943. Fractionation of soil phosphorus. I. Method of extraction. *Indian J. Agr. Sci.* **13**: 29–45.

GHANI, M. O. 1944. Fractionation of soil phosphorus. III. The organic phosphorus fraction. *Indian J. Agr. Sci.* **14**: 261–267.

GHANI, M. O., and ALEEM, S. A. 1943a. Effects of liming on the transformation of phosphorus in acid soils. *Indian J. Agr. Sci.* **12**: 873–882.

GHANI, M. O., and ALEEM, S. A. 1943b. Studies on the distribution of different forms of phosphorus in some Indian soils. I. Surface distribution. *Indian J. Agr. Sci.* **13**: 283–288.

GIESEKING, J. E. 1939. The mechanism of cation exchange in the montmorillonite-beidellite-nontronite type of clay minerals. *Soil Sci.* **47**: 1–13.

GODFREY, C. L. 1951. Distribution and nature of phosphorus in a geo-chrono-sequence of loess derived soils. Ph.D. thesis, Iowa State College, Ames, Iowa.

GORING, C. A. I. 1950. Reactions of biological organic phosphorus compounds with clays. Ph.D. thesis, Iowa State College, Ames, Iowa.

GORING, C. A. I. 1953a. Biological transformations of soil and fertilizer phosphorus: I. Theory and methods. *Soil Sci.* (In Press).

GORING, C. A. I. 1953b. Biological transformations of soil and fertilizer phosphorus: II. Synthesis and mineralization of organic phosphorus. *Soil Sci.* (In Press).

GORING, C. A. I., and BARTHOLOMEW, W. V. 1950. Microbial products and soil organic matter: II. The effect of clay on the decomposition and separation of the phosphorus compounds in microorganisms. *Soil Sci. Soc. Amer. Proc. (1949)* **14**: 152–156.

GORING, C. A. I., and BARTHOLOMEW, W. V. 1951. Microbial products and soil organic matter: III. Adsorption of carbohydrate phosphates by clays. *Soil Sci. Soc. Amer. Proc. (1950)* **15**: 189–194.

GORING, C. A. I., and BARTHOLOMEW, W. V. 1952. Adsorption of mononucleotides, nucleic acids, and nucleoproteins by clays. *Soil Sci.* **74**: 149–164.

GORING, C. A. I., and ZOELLNER, A. J. 1953. Biological transformations of soil and

fertilizer phosphorus: III. Determination of available phosphorus. *Soil Sci.* (In Press).

GRANDEAU, L. 1872. Recherches sur le rôle des matières organiques du sol dans les phénomènes de la nutrition des végétaux. *Compt. rend.* **74**: 988–991.

HALLAM, M. J. 1952. Influence of moisture, aeration and substrate on rates of biological transformations of carbon and nitrogen in soil. Ph.D. thesis, Iowa State College, Ames, Iowa.

HENDRICKS, S. B., 1941. Base exchange of the clay mineral montmorillonite for organic cations and its dependence upon adsorption due to van der Waals forces. *J. Phys. Chem.* **45**: 65–81.

HOCKENSMITH, R. D., GARDNER, R., and GOODWIN, J. 1933. Comparison of methods for estimating available phosphorus in alkaline calcareous soils. *Colorado Agr. Expt. Sta. Tech. Bull.* **2**.

HUDIG, J., and DOMINGO, W. R. 1942. Het organisch gebonden phosphaat in den grond. *Landbouwkund. Tijdschr.* **54**: 633–638.

JACKMAN, R. H. 1949. Mineralization of inositol-bound phosphorus in soil. Ph.D. thesis, Iowa State College, Ames, Iowa.

JACKMAN, R. H., and BLACK, C. A. 1951. Solubility of iron, aluminum, calcium, and magnesium inositol phosphates at different pH values. *Soil Sci.* **72**: 179–186.

JACKMAN, R. H., and BLACK C. A. 1952a. Phytase activity in soils. *Soil Sci.* **73**: 117–125.

JACKMAN, R. H., and BLACK, C. A. 1952b. Hydrolysis of phytate phosphorus in soils. *Soil Sci.* **73**: 167–171.

JAROSZ, W. 1934. De l'hydrolyse des composés phytiques, tirés de graines de chanvre, de féveroles, de lin, de marrons d'Inde, de froment et d'embryons de seigle. *Bull. intern. acad. polonaise Classe sci. math. nat.* **1933 B1**: 123–133.

JEGOROW, M. A. 1912. Zur Kenntnis der Eigenschaften des Phytins. Vorläufige Mitteilung. *Biochem. Z.* **42**: 432–439.

JEGOROW, M. A. 1914. Zur Kenntnis der Eigenschaften des Phytins. II. Mitteilung. *Biochem. Z.* **61**: 41–54.

KAILA, A. 1948. Viljelysmaan orgaanisesta fosforista. *Valtion Maatalouskoetoiminnan Julkaisuja No.* **129**.

KAILA, A. 1949a. Karjanlannan fosforista. *Maatalousteteellinen Aikakauskirja* **21**: 67–82.

KAILA, A. 1949b. Biological absorption of phosphorus. *Soil Sci.* **68**: 279–289.

KARPINSKIĬ, N. P., and ZAMYATINA, V. B. 1933. (Phosphoric acid combined with soil organic matter.) *Proc. Gedroiz Inst. Fertilizers (Moscow)* **2**: 133–147. [*C. A.* **29**: 1922 (1935)].

KAZIEV, M. Z. 1940. (The various forms of phosphorus in serozem soils.) *Doklady Vsesoyuz. Akad. Sel'skokhoz. Nauk im. V. I. Lenina* **1940**, No. 17: 23–24.

KHEIFETS, D. M. 1948. (A method of determining and the content of mineral and organic phosphorus in certain soils of the Soviet Union.) *Pochvovedenie* **1948**: 100–112.

KHVOROV, I. P., and ONOKHAVA, K. YA. 1939. (Changes in the physical and chemical properties of the soil on plowing virgin soil for the planting of grain and on fallowing.) *Trudy Kazakhskogo Nauch.-Issledovatel. Inst. Zemledeliya* **1**: 123–141 [*C. A.* **36**: 4253 (1942)].

KORABLEVA, L. I. 1951. (The influence of systematic manuring and of vegetative cover on the phosphate regime of peat podzolized soils.) *Pochvovedenie* **1951**: 100–114.

KOROLEV, Y. 1910. (Organic phosphorus compounds of the soil.) *Izvest. Moskov. Selsk. Khoz. Inst.* **16**: 1–98.

KOSSEL, A. 1881. Ueber die Herkunft des Hypoxanthin in den Organismen. *Z. physiol. Chem.* **5**: 152–157.

KURCHATOV, P. A. 1936. (Organic phosphorus in soils.) *Vsesoyuz. Nauch.-Issledovatel. Inst. Tabach. i Makhoroch. Prom.* **129**: 33–42.

KURCHATOV, P. A., and PIL, YU. F. 1935. (Organic phosphorus in soils and methods for its quantitative determination.) *Vsesoyuz. Nauch.-Issledovatel. Inst. Tabach. i Makhoroch. Prom.* **119**: 93–98.

KURSANOV, A. 1938. (Determination of inorganic phosphate, phytin, hexose diphosphate, hexose monophosphate and glycerol phosphate in mixtures.) *Biokhimiya.* **3**: 467–480.

LOCKETT, J. L. 1938. Nitrogen and phosphorus changes in the decomposition of rye and clover at different stages of growth. *Soil Sci.* **45**: 13–24.

MADANOV, P. V. 1940. (A method for determining organic phosphorus of the soil.) *Uchenye Zapiski Kazan. Gosudarst. Univ. im. V. I. Ul'yanova-Lenina* **100**, Book 1, No. 3: 53–68.

MAMCHENKO, I. P. 1941. (The influence of phosphatic fertilizers on the humification of organic matter and the transformation of the nitrogen of manure.) *Vestnik. Udob. Agrotekh. Agropochvoved.* **3**: 5–25 [*Soils and Fertilizers* **8**: 112 (1945)].

MAREL, H. W. VAN DER. 1935. Onderzoek naar het voorkomen van organische fosforverbindingen in de grond. *Landbouwkund. Tijdschr.* **47**: 85–87.

MARTIN, J. B., and DOTY, D. M. 1949. Determination of inorganic phosphate. Modification of isobutyl alcohol procedure. *Anal. Chem.* **21**: 965–967.

MATTSON, S., BARKOFF, E., and WILLIAMS, E. G. 1950. Phosphate relationships of soil and plant. IV. Forms of P in the hydrologic soil series of the Dala brown earth and the Unden podzol. *Kgl. Lantbruks-högskol. Ann.* **17**: 121–129.

MATTSON, S., WILLIAMS, E. G., and BARKOFF, E. 1950. Phosphate relationships of soil and plant. III. Forms of P in the Bränналt limed and unlimed podzol series. *Kgl. Lantbruks-högskol. Ann.* **17**: 107–120.

METHA, N. C. 1951. Determination of organic phosphorus in soils. M.S. thesis, Iowa State College, Ames, Iowa.

MULDER. 1844. Ueber die Bestandtheile der Ackererde. *J. prakt. Chem.* **32**: 321–344.

NANNES, G. 1899. Zur Frage über die Verbindungsformen der Phosphorsäure in der Moorerde. *J. Landw.* **47**: 45–48.

NEUBERG, C., and ROBERTS, I. S. 1949. Remarkable properties of nucleic acids and nucleotides. *Arch. Biochem.* **20**: 185–210.

ODYNSKY, W. 1936. Solubility and distribution of phosphorus in Alberta soils. *Sci. Agr.* **16**: 652–664.

PARKER, F. W., and FUDGE, J. F. 1927. Soil phosphorus studies: I. The colorimetric determination of organic and inorganic phosphorus in soil extracts and the soil solution. *Soil Sci.* **24**: 109–117.

PEARSON, R. W. 1940. Determination of organic phosphorus in soils. *Ind. Eng. Chem. Anal. Ed.* **12**: 198–200.

PEARSON, R. W., NORMAN, A. G., and HO, C. 1941. The mineralization of the organic phosphorus of various compounds in soil. *Soil Sci. Soc. Am. Proc.* **6**: 168–175.

PEARSON, R. W., and SIMONSON, R. W. 1940. Organic phosphorus in seven Iowa soil profiles: distribution and amounts as compared to organic carbon and nitrogen. *Soil Sci. Soc. Amer. Proc.* (*1939*) **4**: 162–167.

PETERSON, P. P. 1911. Effect of heat and oxidation on the phosphorus of the soil. *Wisconsin Agr. Expt. Sta. Research Bull.* **19.**

PIERRE, W. H. 1948. The phosphorus cycle and soil fertility. *J. Am. Soc. Agron.* **40**: 1–14.

PIERRE, W. H., and PARKER, F. W. 1927. Soil phosphorus studies: II. The concentration of organic and inorganic phosphorus in the soil solution and soil extracts and the availability of the organic phosphorus to plants. *Soil Sci.* **24**: 119–128.

PINCK, L. A., SHERMAN, M. S., and ALLISON, F. E. 1941. The behavior of soluble organic phosphates added to soils. *Soil Sci.* **51**: 351–365.

PONS, W. A., and GUTHRIE, J. D. 1946. Determination of inorganic phosphorus in plant materials. *Ind. Eng. Chem. Anal. Ed.* **18**: 184–186.

POTTER, R. S., and BENTON, T. H. 1916. The organic phosphorus of soil. *Soil Sci.* **2**: 291–298.

POTTER, R. S., and SNYDER, R. S. 1918. The organic phosphorus of soil. *Soil Sci.* **6**: 321–332.

ROBINSON, R. R. 1937. Soil properties determining the botanical composition of pastures in West Virginia. *J. Agr. Research* **54**: 877–897.

RUSSELL, E. J., and PRESCOTT, J. A. 1916. The reaction between dilute acids and the phosphorus compounds of the soil. *J. Agr. Sci.* **8**: 65–110.

SALONEN, M. 1941. Fosforin esüntymismuodoista suomen maalajeissa. *Acta Agralia Fennica 48.*

SALONEN, M. 1946. Kalkituksen vaikutuksista maaperän organiseen ja helppoliukoiseen fosforiin. *Maataloustieteellinen Aikakauskirja* **18**: 1–10.

SCHARRER, K., and KELLER, B. 1940. Über Verteilung, Mineralisation und Absorption organischer Phosphorsäureverbindungen im Boden. *Bodenkunde u. Pflanzenernähr.* **19**: 109–124.

SCHMIDT, G. 1951. The biochemistry of inorganic pyrophosphates and metaphosphates. *In Phosphorus Metabolism*, Vol. I, pp. 443–475. W. D. McElroy and B. Glass, Editors. Johns Hopkins Press, Baltimore.

SCHMOEGER, M. 1893. Ueber den Phosphor im Moorboden. *Ber. Deut. Chem. Ges.* **26**: 386–394.

SCHOLLENBERGER, C. J. 1918. Organic phosphorus of soil: experimental work on methods for extraction and determination. *Soil Sci.* **6**: 365–395.

SCHOLLENBERGER, C. J. 1920. Organic phosphorus content of Ohio soils. *Soil Sci.* **10**: 127–141.

SCHREINER, O., and LATHROP, E. C. 1912. The chemistry of steam-heated soils. *U. S. Dept. Agr. Bur. Soils Bull.* **89.**

SELIGSON, NIKOLAI. 1930. Verbindungen der Inositphosphorsäuren mit Molybdansäure. *Arch. Pharm.* **268**: 147–151.

SHOREY, E. C. 1911. Nucleic acids in soils. *Biochem. Bull.* **1**: 104.

SHOREY, E. C. 1912. Nucleic acids in soils. *Science* **35**: 390.

SHOREY, E. C. 1913. Some organic soil constituents. *U. S. Dept. Agr. Bur. Soils Bull.* **88.**

SHRIKHANDE, J. G. 1948. Assimilation of phosphorus during the decomposition of plant materials. *Current Sci.* **17**: 364–365.

SMITH, C. R. 1934. Base exchange reactions of bentonite and salts of organic bases. *J. Am. Chem. Soc.* **56**: 1561–1563.

SMITH, D. H., and CLARK, F. E. 1951. Anion-exchange chromatography of inositol phosphates from soil. *Soil Sci.* **72**: 353–360.

SMITH, D. H., and CLARK, F. E. 1952. Chromatographic separations of inositol phosphorus compounds. *Soil Sci. Soc. Amer. Proc.* **16**: 170–172.

SOKOLOV, D. F. 1940. (Determination of organically-combined phosphorus in soils.) *Pochvovedenie* **1940**, No. 3: 118–125.

SOKOLOV, D. F. 1944. (The presence of phosphatide phosphorus in soils.) *Priroda* **1944**, No. 5–6: 105–107.

SOKOLOV, D. F. 1948. (The presence of certain organic phosphorus compounds in soils.) *Pochvovedenie* **1948**, 503–513.

SPIEGEL-ADOLF, M. 1944. Physical chemistry of lipides. *In* Colloid Chemistry, Vol. 5, pp. 1119–1136. J. Alexander, Editor. Reinhold Publishing Corp., New York.

STEWART, J. 1912. Organic phosphorus in the soil. *Orig. Com. 8th Intern. Congr. Appl. Chem.* **15**: 273–300.

STEWART, R. 1910. Quantitative relationships of carbon, phosphorus, and nitrogen in soils. *Ilinois Agr. Exp. Sta. Bull.* **145**.

STOKLASA, J. 1911. Biochemischer Kreislauf des Phosphat-Ions im Boden. *Zentr. Bakteriol. Parasitenk.* (II) **29**: 385–519.

TAYLOR, C. B. 1946. Loss of available phosphate in soil due to microorganisms. *Nature* **158**: 447.

THOMPSON, L. M. 1947. Mineralization of organic phosphorus in Clarion and Webster soils. M.S. thesis, Iowa State College, Ames, Iowa.

THOMPSON, L. M. 1950. The mineralization of organic phosphorus, nitrogen and carbon in virgin and cultivated soils. Ph.D. thesis, Iowa State College, Ames, Iowa.

THOMPSON, L. M., and BLACK, C. A. 1948. The effect of temperature on the mineralization of soil organic phosphorus. *Soil Sci. Soc. Amer. Proc. (1947)* **12**: 323–326.

THOMPSON, L. M., and BLACK, C. A. 1950. The mineralization of organic phosphorus, nitrogen, and carbon in Clarion and Webster soils. *Soil Sci. Soc. Amer. Proc. (1949)* **14**: 147–151.

THOMPSON, L. M., BLACK, C. A., and CLARK, F. E. 1949. Accumulation and mineralization of microbial organic phosphorus in soil materials. *Soil Sci. Soc. Amer. Proc. (1948)* **13**: 242–245.

THOMPSON, L. M., BLACK, C. A., and ZOELLNER, J. A. 1953. Occurrence and mineralization of organic phosphorus in soils, with particular reference to associations with nitrogen, carbon, and pH. *Soil Sci.* (In press).

UMBREIT, W. W., BURRIS, R. H., and STAUFFER, J. F. 1949. Manometric Techniques and Tissue Metabolism. p. 188. Burgess Publishing Co., Minneapolis.

VINCENT, C. 1917. Les formes du phosphore dans les sols granitiques bretons. *Compt. rend.* **164**: 409–411.

VINCENT, V. 1937. Combinaisons organiques du phosphore des sols acides: assimilation par les vegetaux. *Compt. Rend. 17th congr. chim. ind. Paris* **2**: 861–876.

VINCENT, V. 1938. Combinaisons organiques du phosphore dans les sols acides. *In* Recherches sur la Fertilisation Effectuées en 1937 par les Stations Agronomiques. *Ministère Agr. (France) Rapport Annuel* **11**: 38–39.

WEEKS, M. E., and KARRAKER, P. E. 1941. A comparison of various extracting solutions for measuring the availability of phosphorus in soils of known fertility treatment and crop performance. *Soil Sci.* **51**: 41–54.

WHITNEY, R. S., and GARDNER, R. 1936. Notes on estimating available phosphorus by extracting soils with a potassium carbonate solution. *Soil Sci.* **41**: 33–34.

WILLIAMS, C. H. 1950a. Studies on soil phosphorus. I. A method for the partial fractionation of soil phosphorus. *J. Agr. Sci.* **40**: 233–242.

WILLIAMS, C. H. 1950b. Studies on soil phosphorus. II. *The nature of native and* residual phosphorus in some south Australian soils. *J. Agr. Sci.* **40**: 243–256.

WILLIAMS, C. H. 1950c. Studies on soil phosphorus. III. Phosphorus fractionation as a fertility index in south Australian soils. *J. Agr. Sci.* **40**: 257–262.

WITTCOFF, H. 1951. The Phosphatides. Reinhold Publishing Corp., New York.

WRENSHALL, C. L., and DYER, W. J. 1939. A method for the determination of *organic phosphorus in soils and soil extracts. Canadian J. Research* **17B**: 199–205.

WRENSHALL, C. L., and DYER, W. J. 1941. Organic phosphorus in soils: II. The nature of the organic phosphorus compounds. A. Nucleic acid. B. Phytin. *Soil Sci.* **51**: 235–248.

WRENSHALL, C. L., DYER, W. J., and SMITH, G. R. 1940. Recent studies on the nature of soil organic phosphorus. *Sci. Agr.* **20**: 266–271.

WRENSHALL, C. L., and MCKIBBIN, R. R. 1937. Pasture studies. XII. The nature of the organic phosphorus in soils. *Canadian J. Research* **15B**: 475–479.

YOSHIDA, R. K. 1940. Studies on organic phosphorus compounds in soil; isolation of inositol. *Soil Sci.* **50**: 81–89.

YUEN, S. H., and POLLARD, A. G. 1951. The availability of soil phosphate. I.—Examination of the soil solution with special reference to the fixation of phosphate. *J. Sci. Food. Agr.* **2**: 186–192.

CHAPTER VI

The Development, Evaluation, and Use of Soil Tests for Phosphorus Availability

W. L. NELSON, A. MEHLICH and ERIC WINTERS

I. Introduction

Soil tests for available phosphorus have been under investigation for a considerable period of time and have aroused the interest of a large number of research workers. Even though a voluminous literature on the subject has been developed, many problems relating to the testing of soils for available phosphorus remain unsolved. Periodic reviews and appraisals of soil-testing studies indicate the extent of current usage of different soil-testing methods and something about the general reliability of the tests. Furthermore, such reviews and appraisals should help identify more clearly some of the major problems needing attention and may indicate promising lines of attack.

An objective of soil tests for available phosphorus is to estimate the phosphorus fertility level of soils. Such estimates are intended to be helpful in the prediction of fertilizer needs of a field. A more general objective of soil testing may be realized through the preparation of summaries of soil test results over an area to estimate fertility levels. Information about fertility levels of a region will be helpful in long-range planning of fertilizer production facilities.

1. Biologically Available and Chemically Soluble Forms of Phosphorus in Soils

The development of soil test methods for phosphorus has proceeded in various directions, changing with the knowledge of the mechanism of phosphate sorption by plants and with the knowledge of the soil factors influencing the availability of phosphorus. In view of the observations that plants can utilize water-soluble, carbon dioxide-saturated water-soluble, acid-soluble, and exchangeable sources of phosphorus, the soil test methods in use at the present time take cognisance of these various conditions. The development of chemical methods is complicated by the fact that plants differ in their ability to obtain phos-

phorus from the soil. Such factors as the character of the root system with regard to its degree of ramification throughout the soil, its rate of growth, the total phosphorus requirement, metabolically produced CO_2, and exchangeable H of plant roots vary substantially among different plant species. For example, if the principal source of phosphorus is a relatively insoluble form of calcium phosphate, the plant species having the greater power to mobilize calcium will secure phosphorus more readily than the plant species having a lower energy for the mobilization of calcium. Other factors would, however, come into play if the principal source of phosphorus is in exchangeable form.

There is good evidence to indicate that phosphorus is sorbed by plant roots mainly as $H_2PO_4^-$. In the soil pH range 4.0 to 9.0 within which plants usually grow, the predominant ions of phosphorus in solution are $H_2PO_4^-$ and $HPO_4^=$. The pH value in the immediate vicinity of active plant roots is usually somewhere in the neighborhood of 5, as a result in large measure of the excretion of metabolic CO_2 at the root surface. The dominant ion of phosphorus in this immediate root zone must be $H_2PO_4^-$ (Bates and Acree, 1943). Even though this suggests that an estimate of water-soluble phosphorus in the soil should give a good measure of the level of phosphorus available to the plant, this is not necessarily true. Factors which affect the transformation of water-insoluble phosphate to water-soluble phosphate might affect the so-called "phosphorus-supplying power" of the soil. This would permit plants in some soils to obtain an adequate amount of phosphorus even though the water-soluble level might be low.

According to Russell and Russell (1950), some of the more important phosphorus-containing materials are as follows:

1. Apatite, both the hydroxy- and fluorapatite species.
2. Calcium and magnesium phosphates which vary in composition. It is difficult to give any specific formula that would represent the group of calcium-magnesium phosphates in the soil.
3. Iron and aluminum phosphates, including the phosphates bound or "sorbed" on the surface of hydrated iron and aluminum oxides.
4. Organic phosphates, such as phytin and other inositol phosphates, nucleic acid, and its derivatives.

Many attempts have been made to study and describe the various forms of phosphorus that may be present in soil. Since the time of Daubeny (1845), many methods have presumed to measure the quantity of an "available" nutrient present in a given soil. The fallacy of this assumption has been pointed out by Bray (1937), who emphasized the importance of determining all, or a known proportion, of a nutrient form or forms of the phosphorus present. Bray further suggests that the

soil test method to be developed should measure the predominant forms or form of a nutrient from which the plant roots meet their requirements during a growing season.

2. *Soil Factors Influencing Solubility of Phosphorus*

The soil pH greatly affects the amount of phosphorus that is transformed to the water-soluble condition. It is generally agreed, for example, that raw rock phosphate is less available to most crops in neutral and alkaline soils than it is in moderately acid soils. The amount of organic matter in the soil and the rate at which it decomposes may influence phosphorus availability. This is true particularly in the case of calcium phosphate forms, since the CO_2 produced may tend to exert a solvent action.

The type of colloid and its associated compounds probably determines in part the form to which fertilizer phosphorus reverts after application. Soils containing colloids of the montmorillonitic and organic types would fix less phosphorus as iron and aluminum complexes than the kaolinitic and hydrous oxide types of colloid. These and other soil factors which cannot be discussed in further detail here all influence the availability of soil supplies of phosphorus to plants.

II. Development of Soil Tests for Phosphorus Availability

A large number of soil-testing procedures have been developed for the measurement of available phosphorus in soils. Some of the procedures are very similar, although differing in detail. Others represent extremes in variation. The procedures may be grouped for convenience into two broad categories, each of which can be subdivided: (1) extraction methods and (2) biological methods.

1. *Extraction Methods*

The extraction methods have been grouped into four categories: (a) water, (b) carbon dioxide-saturated water, (c) acids, bases, salts, and buffered solutions, and (d) electrodialysis and ion exchangers.

a. Water. A large number of workers including Blenkinsop (1938), Burd and Murphy (1939), and Bingham (1949) have developed methods based on extraction of soil phosphorus with water. Under some soil and crop conditions, this procedure has given satisfactory prediction of crop response to phosphorus fertilization. Water as an extracting reagent for phosphorus is employed on sandy soils, such as in the citrus fruit areas and the organic Everglades soils of Florida (Forsee, 1950). Under these conditions the conversion of added soluble phosphorus into insoluble forms is not great. Hence, the relatively large portion of the

PAU CENTRAL LIBRARY
Acc: No: G 790

phosphorus remaining in soluble forms serves as the principal source of phosphorus for plants.

Under many soil conditions, water extracts fail to give a good correlation between soil test results and crop response. One reason is probably related to the unbuffered character of the water. This results in the pH of the final solution, after soil extraction, being influenced greatly by the pH of the soil. Another major objection to the use of water is the frequent failure to obtain a clear extract. Whether the extract is clear or not depends to a great extent upon the electrolyte content of the soil. Conversely the electrolyte content affects the solubility of phosphorus. The presence of KCl, for example, increases the solubility of the alkaline earth phosphates but decreases the solubility of iron and aluminum phosphates (Mattson *et al.*, 1950).

b. Carbon Dioxide-Saturated Water. The use of CO_2-saturated water has long been advocated for soil testing on the basis that plant roots produce CO_2 (Mitscherlich, 1930). McGeorge (1939) found that the solubility of phosphorus in alkaline soils increased with increasing concentration of CO_2 in the water. He also found that the amount of phosphorus dissolved was influenced by the soil:solution ratio.

Machigin, quoted by Brind (1950), found that bubbling CO_2 for two hours through a 1:100 soil:water suspension gave a better correlation with crop response to phosphorus than did the nitric acid method of Von Sigmond (1929) or the 1 per cent potassium carbonate method of Das (1930). Stanberry (1949) found CO_2 extraction a satisfactory substitute for the Neubauer method on a Serozem soil. Recent work by Olson, reported in this monograph, reveals that alkali carbonate and bicarbonate solutions are more satisfactory than CO_2.

c. Other Acids, Bases, Salts, and Buffered Solutions. (1) General considerations. As in the case of water and CO_2, the selection of organic acids as extracting solutions has been based on the assumption that plant roots excrete organic acids and that organic acids have a solvent power comparable to CO_2-saturated water. The selection of inorganic acids, however, is largely based on analytical expediency, in that reagents are chosen which interfere as little as possible in the colorimetric determination of phosphorus by means of the Denigés molybdenum blue method. This, however, may not be desirable, as the selection of the reagent should be based on the nature of the phosphorus present in the soil.

Recent work on the chemical methods for the determination of phosphorus in the soil has been reviewed by Brind (1950). The organic acid extractions proposed and still widely used are: (a) the citric acid methods of Dyer, and modified by König and Hasenbäumer (described

by Lemmerman and Fresenius, 1934, by Das (1930), and by Lemmerman and Fresenius (1934); (b) the lactic acid method of Egner (1941) and various modifications as suggested by Riehm (1940)—see Brind (1950); and (c) the acetic acid method of Hibbard (1931).

The mineral acids used are: 0.01 *N* HNO_3 by Von Sigmond (1929), 0.2 *N* HNO_3 by Fraps (1909), 0.314 *N* HCl by Baver and Bruner (1939), 0.7 *N* HCl by Olson (1946), 0.2 *N* H_2SO_4 by Bondorff (see Brind, 1950), 0.01 *N* H_2SO_4 by Kerr and Stieglitz (1938), and a mixture of 0.05 *N* HCl and 0.025 *N* H_2SO_4 by Mehlich (unpublished). Many investigators use buffered solutions. The most widely used are 0.002 *N* H_2SO_4 buffered at pH 3 with $(NH_4)_2SO_4$ (Truog, 1930; Peech *et al.*, 1947; Mukherjee, 1941; Rubins and Dean, 1946), and acetic acid buffered near pH 4.8 with sodium acetate (Morgan, 1937; Lunt *et al.*, 1950; Peech and English, 1944; Dahlberg and Brown, 1932; Henda, 1950) and with ammonium acetate (Florida Station, Soil Test Work Group, 1951). Beater (1949) used *N*/21 H_2SO_4 buffered with sodium borate at pH 1.5; Bray (1948) used HCl buffered with NH_4F; Ghani (1943) used acetic acid in the presence of 8-hydroxyquinoline; and Cooke (1951) used 0.5 *N* acetic acid at pH 2.5 mixed with various complexing agents.

Alkali extractions are used on some red soils, and 0.5 *N* NaOH has been recommended by Jones (1949). Other alkali solutions are the 1 per cent potassium carbonate method of Das (1930) and the calcium bicarbonate method of Dirks and Scheffer (1928). According to Laatsch (1941), solutions of $KHCO_3$ were effective in the replacement of exchangeable phosphorus, whereas solutions of either K_2SO_4, KCl, or carbon dioxide-saturated water were not. The latter was effective, however, in releasing phosphorus from apatite-like phosphates.

(2) *Factors to be considered in the development of soil tests:* (a) Refixation of Phosphorus During Extraction. A review of most of the papers dealing with this subject has been made by Wild (1950a). Even though a definite identification of the forms of phosphorus present in a given soil may have been ascertained, the interpretation of the test may be subject to error because of secondary reactions taking place during extraction. These secondary reactions generally involve a reduction of the phosphate ion concentration or "re-fixation." This readsorption of phosphorus may be caused either by a reduction in the H ion concentration of the acid extractant or by a fixation by various metallic oxides or hydrates of iron, aluminum, titanium, and manganese. To overcome the effect of the former, either the extracting solution must be sufficiently strongly buffered or the soil:solution ratio employed must be wide enough to prevent appreciable fluctuation in pH. Hence, in using

the lactic acid method of Egner (1941). Riehm (1940) employs a 1 g. sample of soil in place of the usual 5 g. sample whenever the soil contains free $CaCO_3$.

In order to reduce the effect of re-fixation by the metallic oxides during the extracting process, complexing agents have been used successfully. The most extensive study of this nature has been reported by Cooke (1951). Using 0.5 *N* acetic acid at pH 2.5 as the extracting solution and adding various metallic oxides, he found that the percentage fixation of added phosphorus was reduced by the addition of complexing reagents. A portion of these data are reproduced in Table I. The data

TABLE I

THE VALUE OF REAGENTS IN PREVENTING FIXATION OF ADDED PHOSPHATE BY HYDROUS OXIDES IN ACID SUSPENSION[a]

Oxide	*Amount, grams*	*Reagent*	*Amount, grams*	*Percentage fixation of added phosphate*	
				Without reagent	*With reagent*
TiO_2	0.100	8-Hydroxyquinoline	0.75	96	74
TiO_2	0.025	Selenious acid	0.25	93	5
Fe_2O_3	0.050	8-Hydroxyquinoline	0.50	100	86
Fe_2O_3	0.050	Citric acid	1.00	100	12
Fe_2O_3	0.050	Selenious acid	0.25	100	18
Al_2O_3	0.030	Morin (in alcohol)	1.00	90	29
Al_2O_3	0.030	Quinalizarin (in alcohol)	1.00	80	36
Al_2O_3	0.030	Citric acid	1.00	68	11
Al_2O_3	0.030	Oxalic acid	1.00	68	14
Al_2O_3	0.030	Ammonium fluoride	1.00	71	12
Al_2O_3	0.030	Potassium ferrocyanide	1.00	68	27
MnO_2	0.100	Selenious acid	1.00	35	18

[a] Cooke (1951).

show selenious acid, citric acid, oxalic acid, and ammonium fluoride to be very effective, potassium ferrocyanide, quinalizarin and morin to be moderately effective, and 8-hydroxyquinoline to be least effective in reducing phosphorus fixation.

Cooke found further that kaolinite, halloysite, and bentonite fixed very little phosphorus at either pH 2.5 or 4.5 and that selenious acid did not retard fixation. However, when $CaHPO_4$ was added to latosolic soils, fixation at pH 2.5 was substantial only in the absence of selenious acid.

(b) Effect of the Anion on Phosphorus Dissolved. The solution of phosphate from calcium phosphate by dilute acids is straightforward,

unless, as has been pointed out, re-fixation occurs. The solution of phosphorus from the exchangeable forms or from iron or aluminum phosphates depends, however, upon the nature of the anion of the extractant. Kurtz *et al.* (1946) found the "replacing" ability of anions for sorbed phosphate to be in the increasing order: chloride, sulfate, thiocyanate, acetate, borate, bicarbonate, citrate, oxalate, fluoride. In view of the high efficiency of the fluoride ion in dissolving phosphate, Bray (1948) recommended the use of this reagent together with HCl as an extractant. The reagent recommended for replacing the sorbed phosphate consisted of 0.03 *N* NH_4F in 0.025 *N* HCl, and the reagent for the combined acid-soluble and sorbed forms consisted of 0.03 *N* NH_4F in 0.1 *N* HCl.

Seatz (1949), working with thirty-two soils which contained from 25 to 50 per cent kaolinite in the clay fraction, compared a number of extracting solutions for their efficiency in dissolving phosphate. The average of these data is given in Table II. The results show that neutral

TABLE II

AMOUNT OF PHOSPHORUS EXTRACTED BY SEVEN DIFFERENT REAGENTS FROM 32 SOILS[a]

	Pounds of phosphorus per acre extracted by:						
	0.03 N NH_4F in 0.1 N H_2SO_4	*0.03 N NH_4F in 0.1 N HCl*	*0.1 N NH_4F*	*0.1 N H_2SO_4*	*0.1 N HCl*	*0.1 N NaOH*	*0.002 N H_2SO_4*
Average	80.0	64.3	8.3	69.8	43.7	43.4	87.3
Range	24–200	16–204	3–20	11–174	3–228	15–132	6–136

[a] Seatz (1949).

0.1 *N* NH_4F dissolves the least and that 0.03 *N* NH_4F in 0.1 *N* H_2SO_4 releases the most phosphate. The Bray extracting solution releases less phosphorus than 0.1 *N* H_2SO_4 but more phosphorus than 0.1 *N* HCl. Seatz also studied the relative efficiency of some of these reagents on laboratory preparations of iron and aluminum phosphate. A portion of these results are shown in Fig. 1. There is little difference between HCl and H_2SO_4, with aluminum phosphate. With iron phosphate, however, H_2SO_4 is more effective than HCl in dissolving phosphorus. In both systems, the acidified NH_4F lies between HCl and H_2SO_4, whereas neutral NH_4F was least effective.

The problem of the effect of the extracting solution on the solution of phosphate from soils containing different types of colloids was studied by one of the authors (Mehlich). In developing a soil test for North

Carolina soils, it had been deemed expeditious and economical to select an extracting solution in which calcium, magnesium, phosphorus, and potassium could be measured in a single extract. The extractant in the "Universal" system (Morgan, 1937) consists of a mixture of acetic acid and sodium acetate adjusted to pH 4.8. This extracting solution, or minor modifications thereof, is widely used in the northeastern region of the United States (Soil Test Work Group, 1951). Though this extracting solution is relatively efficient in removing the exchangeable metal cations (Peech and English, 1944), it has failed to extract measurable quantities of phosphorus from many high phosphate fixing soils

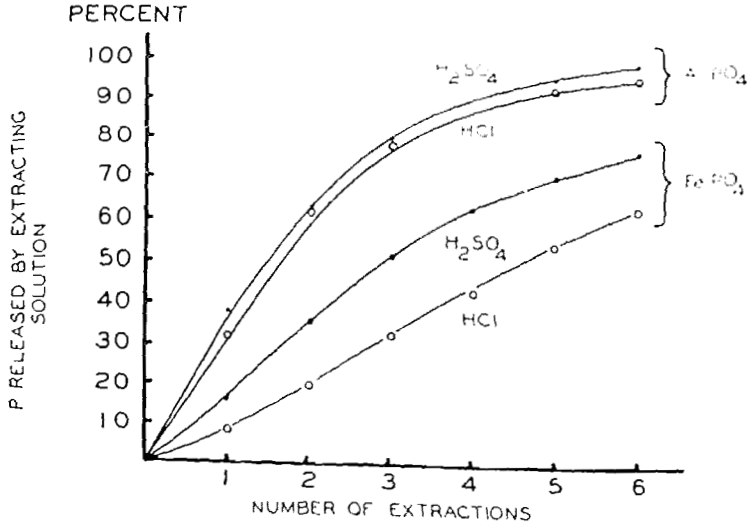


FIG. 1. Relative effectiveness of H_2SO_4 and HCl in extracting phosphorus from $FePO_4$ and $AlPO_4$ (Seatz, 1949).

of the Piedmont and Mountain regions of North Carolina. Sodium perchlorate and perchloric acid were also tried without further success. Next 0.05 *N* HCl was tried. Although this extracting solution appeared to be somewhat more promising, experimental results in the laboratory and greenhouse indicated too low a recovery of phosphorus from high phosphate fixing soils adequately supplied with available phosphorus.

A search for a reagent which would extract a larger proportion of the difficultly available phosphorus was, therefore, undertaken. Data in Table III show the relative efficiency of various reagents in extracting phosphates from soils of high and low phosphorus fixing capacity. The results show that neither hydrochloric nor perchloric acid is as effective as sulfuric acid in extracting phosphorus from the Cecil soils. There is little difference among these three reagents as regards the White Store

soil. Lactic acid extracts more phosphorus than does HCl from the Cecil soils but not from the White Store soil. Mixtures of HCl with H_2SO_4, $(NH_4)_2SO_4$, or NH_4F are also very effective extractors of phosphorus. Ammonium molybdate, lactic acid, and citric acid in mixtures with HCl do not remove much more phosphorus than HCl alone.

TABLE III

PHOSPHORUS BROUGHT INTO SOLUTION BY VARIOUS REAGENTS

Reagents	Soil and treatment					
	Cecil-R[a]		Cecil-W[b]		White Store[c]	
	Non-phosphated	Phosphated	Non-phosphated	Phosphated	Non-phosphated	Phosphated
	P_2O_5, pounds/acre					
0.05 *N* hydrochloric acid	4	22	8	50	148	412
0.05 *N* sulfuric acid	15	70	24	142	153	435
0.05 *N* perchloric acid	6	15	5	36	119	435
1% lactic acid	14	58	15	75	153	313
0.05 *N* HCl + 1% lactic acid	13	27	12	43	110	313
0.05 *N* HCl + 0.025 *N* H_2SO_4	8	88	26	142	174	435
0.05 *N* HCl + 0.025 *N* $(NH_4)_2SO_4$	8	84	26	133	179	389
0.05 *N* HCl + 0.05 *N* $(NH_4)_2SO_4$	9	90	29	147	174	389
0.05 *N* HCl + 0.06 *N* NH_4F	9	88	32	153	231	389
0.05 *N* HCl + 0.025 *N* $(NH_4)_2MoO_4$	12	43	26	48	39	110
0.05 *N* HCl + 0.01 *N* H_3BO_3	8	22	6	43	133	435
0.05 *N* HCl + 0.05 *N* citric acid	7	38	15	71	142	435

[a] Cecil-R is from Rutherford County, N. C., and is known to fix large quantities of phosphorus. The colloid fraction of this soil contains about 45% kaolinite and 30% gibbsite (Coleman *et al.*, 1949).

[b] Cecil-W is from Wake County, N. C., and is known to fix only moderate amounts of phosphorus. The colloid fraction of this soil is 70% kaolinite (Coleman *et al.*, 1949).

[c] White Store is from Chatham County, N. C., and is known to fix very little phosphorus. The colloid fraction of this soil contains about 70% montmorillonite and 20% kaolinite (Mehlich and Colwell, 1943).

These studies were continued with the phosphated soils using 0.075 *N* HCl, 0.05 *N* HCl + 0.025 *N* NH_4F, and 0.05 *N* HCl + 0.025 *N* H_2SO_4. The samples were shaken for 5 minutes, centrifuged, decanted, and again shaken with fresh solvent for 5 minutes. This was repeated five times. The cumulative amounts removed, expressed as pounds P_2O_5 per acre, are shown by the results in Fig. 2. All three extractants were about equally effective with White Store soil. With the two Cecil soils, however, HCl released less phosphorus than the mixtures. Although the amounts of phosphorus applied to both the Cecil soils (2800

lb. P_2O_5 an acre basis) were the same, approximately 50 per cent of the phosphorus added was released after five extracts from Cecil-W whereas only 14 per cent was released from Cecil-R, with the HCl-H_2SO_4 mixture. The White Store soil received only 1400 lb., but all of this was removed by two extractions.

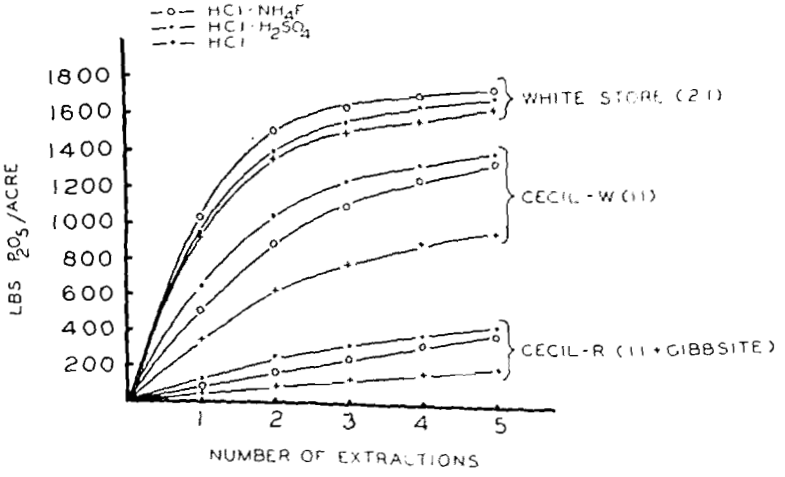


FIG. 2. Effect of soil type and extractant on solution of added phosphate.

Wild (1950b) also has shown that the greatest relative effect of SO_4 ions is at very low concentrations, that is, less than 0.02 *N*. This phase of the problem has been further investigated by adding increasing amounts of Na_2SO_4 to 0.05 *N* HCl and then measuring the phosphorus extracted from the Cecil-R, Cecil-W, and White Store soils studied. The results, shown in Table IV, reveal a large initial increase, followed by

TABLE IV

THE EFFECT OF INCREASING CONCENTRATIONS OF Na_2SO_4 ON THE SOLUBILITY OF SOIL PHOSPHORUS IN HCl

Extracting solution	*Soil and Treatment*		
	Cecil-R	*Cecil-W*	*White Store*
	P_2O_5, pounds/acre		
0.05 *N* HCl	22	50	148
0.05 *N* HCl + 0.05 *N* Na_2SO_4	64	126	172
0.05 *N* HCl + 0.10 *N* Na_2SO_4	64	134	180
0.05 *N* HCl + 0.5 *N* Na_2SO_4	88	148	180
0.05 *N* HCl + 1.0 *N* Na_2SO_4	96	164	207

a gradual increase, in the amount of phosphate extracted with increasing concentration of $SO_4^=$.

These results are in agreement with those of Mattson *et al.* (1950) and Wild (1950b), who have shown that larger amounts of phosphate remain in an acid solution when sulfate salts are added. Mattson's data show that these effects are particularly striking with soils of high iron contents. The data of Cooke (1951) (see Table I) likewise point in the same direction, in that the sulfate ion may have the same effect as the selenate ion. For a detailed explanation of these effects, the reader is

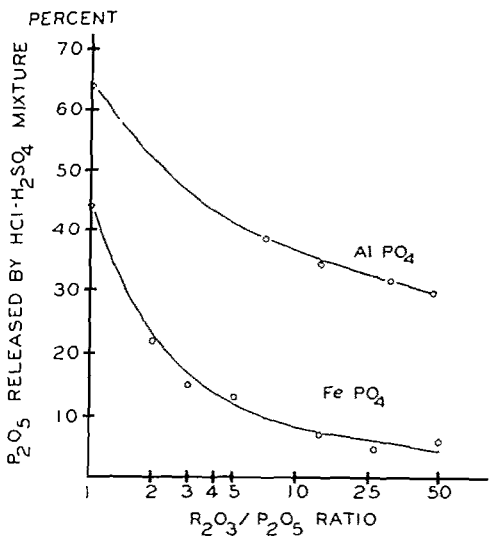


FIG. 3. Effect of R_2O_3 : P_2O_5 ratio on the phosphorus dissolved with an HCl–H_2SO_4 mixture in iron and aluminum systems.

referred to the original papers of the above authors, and, for a general review of the effect of complexing ions, to the papers by Wild (1950a) and Struthers and Sieling (1950).

In the experiment by Seatz the R_2O_3:P_2O_5 ratio of the synthetic phosphates was near 1. In order to study the solution of phosphate over a wider range of R_2O_3:P_2O_5 ratios, increasing amounts of iron and aluminum oxide hydrates, prepared by the addition of NH_4OH to $FeCl_3$ and $AlCl_3$, were treated with 0.5 milliequivalent $PO_4^=$ as H_3PO_4. The phosphate was then extracted with three successive extractions with the 0.05 *N* HCl–0.025 *N* H_2SO_4 mixture. These results are presented in Fig. 3. With increasing R_2O_3:P_2O_5 ratios, the phosphate dissolved decreases in both the iron and aluminum systems. Solution from the aluminum systems is, however, greater than that from the iron systems,

d. Electrodialysis and Ion Exchangers. The older literature pertaining to electrodialysis has been covered by Goodwin (1935). The method is used extensively at the New Jersey Agricultural Experiment Station (Purvis and Hanna, 1949).

Use of cation exchangers has been reported by Bondorff and Damsgaard-Sørensen (1942). The reaction with $Ca(HPO_4)_2$, for example, is as follows: $X\text{–}Na + Ca(HPO_4)_2 \rightarrow X\text{–}Ca + Na_2HPO_4$. After the colloid is separated by centrifuging, the water-soluble phosphorus is then determined. Unpublished data by the Danish Heath society show that this method gives a higher correlation coefficient with crop response than have the Egner and several other chemical methods. The method fails to extract any measurable amount of phosphorus from soils having a high phosphorus fixing capacity, as shown by Coleman (unpublished data). Under such conditions an anion exchanger appears more promising. The reaction would be as follows: $R \cdot OH^- + soil \cdot Al$ or $(FeO)^+H_2PO_4^- \rightarrow R^+ \cdot H_2PO_4^- + soil \cdot Al$ or $(FeO)^+OH^-$. In the case of the anion exchanger, the necessity for the separation of the anion exchanger from the soil and the subsequent replacement of $H_2PO_4^-$ from the exchanger might render this method too cumbersome for rapid soil test work.

2. *Biological Methods*

a. Higher Plants. The methods involving higher plants have been reviewed by Vandecaveye (1948). The field plot technique is, of course, the oldest method, but it is not adapted to extensive application. Biological methods involving growing plants in small quantities of soil in the greenhouse help to bridge the gap between soil analysis and field experiments. In this type of method, the comparative yields and/or uptake of plant nutrients from treated and untreated portions of the soil are usually taken as a measure of plant nutrient status.

In the pot method developed by Mitscherlich (1930), the yield of oats without phosphorus expressed as the percentage of the maximum yield or yield with phosphorus is used as a measure of the phosphorus level in the soil. Bray (1948) has used the Mitscherlich concept in part in calibrating soil tests for phosphorus under Illinois conditions. Vandecaveye (1948) also discusses Jenny's (Jenny *et al.*, 1950) modification of the Mitscherlich method, in which romaine lettuce was used.

The seedling method proposed by Neubauer and Schneider (1923) is based on the amount of phosphorus taken up by rye from 100 g. of soil in 17 days. This method has been extensively used as a reference method for the calibration of chemical methods, notably in Germany.

This method was at one time the "official method" in that country, but it has been subsequently displaced by Egner's lactate method. A detailed discussion of the seedling method is given by Vandecaveye (1948).

Fried and Dean (1952) have presented the concept that a plant having two sources of a nutrient will absorb its nutrients from each of these sources in direct proportion to the amounts available. This has the following logical consequence: the quantity of available nutrient in the soil can be determined in terms of a standard, provided that the proportion of the nutrient in the plant derived from this standard is determined. This can be done using a standard tagged with P^{32}. The mathematical expression of this relationship is as follows:

$$A = \frac{B(1 - y)}{y}$$

where A = amount of nutrient available in the soil, B = amount of nutrient in the standard, and y = proportion of the nutrient in the plant derived from the standard (see Chapter II).

Plant analysis is another method by which the phosphorus level in the soil can be measured indirectly. Ulrich (1948) has reviewed the literature and discussed this method in detail. Plant tissue tests are a more rapid method of analysis and are also used as an indication of the phosphorus status of soils. Krantz *et al.* (1948) have reviewed and discussed these tests. In many respects, the plant should be a good indicator of the soil environment as it tends to integrate all factors. Of course, time and method of sampling, plant species, and weather will all affect plant composition.

b. Microbiological. The premise in using microorganisms as a measure of the phosphorus level is that their requirements for phosphorus are much the same as those of higher plants. Methods based on this principle have been reviewed by Vandecaveye (1948). Butkewitsch (1909) was one of the first to suggest the use of *Aspergillus niger* as a biological indicator of the amount of available phosphorus and potassium in soils. Apparently unaware of this work, Pantanelli (1924) suggested the use of *A. niger*, *A. oryzae*, and *A. flavus* for testing the phosphorus level of soils. He used the phosphorus content of the mycelium as an index of available phosphorus. Benecke and Söding (1928) used *Cladosporium herbarum* and *Stichococcus* in addition to *A. niger*. The *A. niger* method was extensively developed by Niklas *et al.* (1930). Smith *et al.* (1932) concluded that the citric acid present in the medium, which was necessary for the partial sterilization of the soil, was largely

responsible for the solution of soil phosphorus in the *A. niger* method. The results suggest that similar information could probably be obtained with a simple citric acid extract of the soil. This objection was in part overcome when Sekera and Schober (1934) proposed the use of tannic acid in place of citric acid. This modification also included the use of a parallel culture to which a known amount of phosphorus was added. The ratio of the weights obtained from this pair of cultures was used as an index of phosphorus needs.

One of the biological tests involving the use of the natural soil (non-sterilized) is the Winogradsky and Ziemiecka (1927) or soil-plaque method employing *Azotobacter*. This method has been extensively studied with calcareous soils by Hockensmith *et al.* (1933). The method is not applicable to soils below pH 5.0, since this organism does not tolerate excess acidity. In order to develop a biological test which could be used on a natural soil and over a wide range of reaction, Mehlich *et al.* (1934) proposed the use of *Cunninghamella blakesleeana*. This organism will not only grow over a wide range of reaction (pH 4 to 9), but it also has the advantage that it will utilize various forms of organic phosphorus (Mehlich, 1939). In most of the comparisons with methods involving plants the *Cunninghamella* method has compared favorably (Reuszer, 1936; Mooers, 1938; Long, 1947).

III. Correlation of Soil Tests with Plant Growth

The value of a soil test is determined by the accuracy with which that test can be used in the prediction of crop response to fertilization. Correlation of soil test and crop response data has not proven an easy task. Some of the procedures and data relating to such correlation will be discussed in this section, and a limited evaluation of some of the current soil tests will be suggested on the basis of available data. Research needed to help develop better correlations between soil tests and crop response data will be outlined.

1. Correlating Soil Test and Crop Response Data

Crop response to phosphorus fertilization on a given soil may be investigated in either field or greenhouse experiments. Many workers attach greater practical significance to field experiments. Only two treatments are necessary to make a qualitative estimate of crop response (Bray, 1948). One treatment should provide the essential nutrients in such amounts that there is neither a deficiency nor harmful excess of any material. The second treatment is the same except that phosphorus is omitted. Control of water, insects, diseases, weeds, tillage, etc., should be such as to assure favorable growth conditions. If the yield produced

by the first treatment is significantly higher than that produced by the second, the crop is said to respond to phosphorus on that soil.

Information as to the degree of crop response, as well as an estimate of the quantity of phosphorus fertilizer that should be applied, can be obtained if several rates of phosphorus are included. Factorial designs, in which the rates of several nutrients are varied, may be preferable where an estimate of the quantity of phosphorus to apply is to be made.

No discussion is needed here in regard to such usual experimental techniques as careful selection of uniform plot areas, replication, and randomization of treatments, all of which when properly carried out help increase the reliability of the results.

Adequate sampling of the area where field studies are conducted is important, and the samples should be carefully prepared for future laboratory studies on soil testing.

Several methods have been used in the actual correlation of the crop response and soil test data. Only two examples of correlation procedures will be discussed here.

a. Bray's Percentage Yield Concept. The yield levels and absolute differences in yield between treatments may vary greatly because of differences in soil productivity and seasonal effects. Bray (1948), following Mitscherlich (1930), has suggested that the inconvenience of dealing with a wide range in absolute yield differences can be eliminated by expressing crop response in percentage values. The yield obtained with the treatment which included no phosphorus is expressed as a percentage of the yield on the fully treated plot,

$$(\text{No P yield}/\text{P yield}) \times 100$$

Thus, the lower the percentage yield value, the greater the response to phosphorus.

Data obtained on the response of tomatoes by Arnold and Schmidt (1951) are shown in Figs. 4 and 5. Plotting the no P yields as a percentage of the maximum rather than plotting actual responses gives a much better relationship. Bingham (1949) used the same procedure in processing some greenhouse data on the response of lettuce to fertilizer additions. Long (1947) has followed the procedure suggested by Bray in presenting some soil test-crop response correlations. Unless phosphorus fertilizer is used at several rates, however, it is difficult to judge how closely the yield of the full treatment approaches the maximum.

The data expressed as percentage yields are suitable for presentation graphically, or they may be studied for their fit to the Mitscherlich

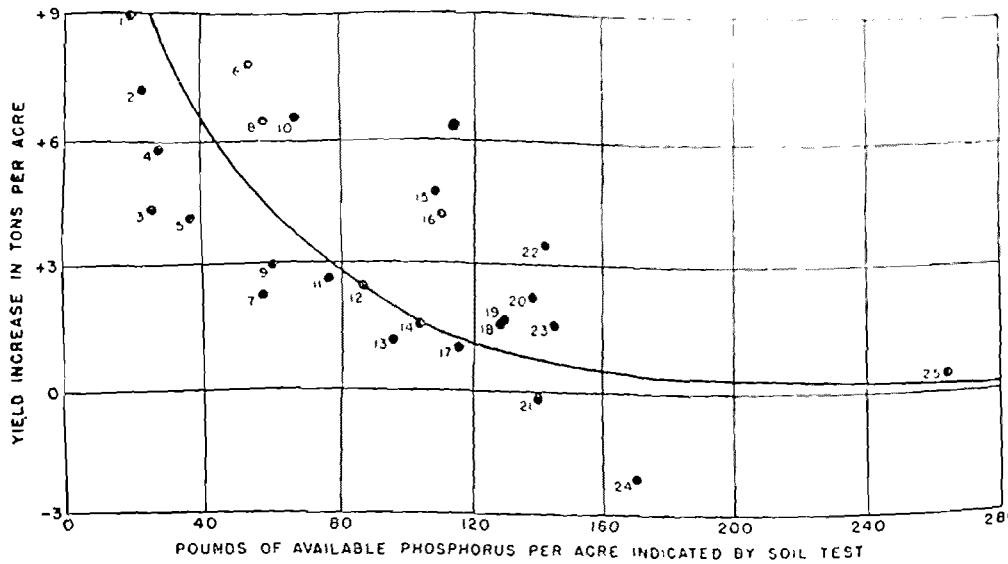


FIG. 4. Relationship between available phosphorus in soil and yield increase of tomatoes obtained with applications of superphosphate (Arnold and Schmidt, 1951).

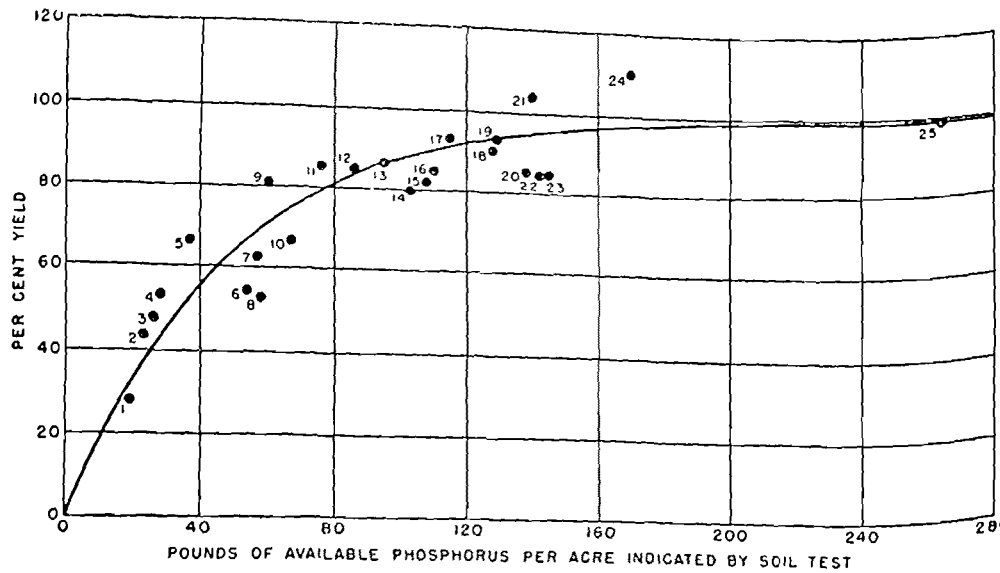


FIG. 5. Relationship between available phosphorus in soil and yield of tomatoes on NK plots computed as a percentage of NPK plots (Arnold and Schmidt, 1951).

growth equation. Mitscherlich's equation was modified by Bray (1948) as follows:

$$\log (A - y) = \log A - c_1 b_1$$

where A = the LPK yield, y = the LK yield, b_1 = the phosphorus test value on the LK plot, and c_1 = the proportionality constant. By solving

for c_1 on each field and averaging the values, a mean c_1 value is obtained for the crop in question.

It is well recognized that crops differ greatly in their ability to grow well at any given level of phosphorus availability. Bray (1948) and Long (1947, 1951) both grouped their data by crops before preparing the graphs and developing the correlations between crop response and soil test results. Bray (1948) found that the c_1 value varied considerably among wheat or clovers, corn, and soybeans or oats. Long (1947) found that responses of wheat to phosphorus applications were better correlated with the soil test for phosphorus than were the cotton responses. Irish potatoes depend heavily on fertilizer phosphorus and Nelson and Hawkins (1947) found appreciable response to phosphorus even on soils containing 850 pounds of available P_2O_5 as determined by the Truog method.

b. Critical Level of Available Phosphorus. Several authors have approached the problem of correlation by putting the soil test results for the responsive soils in one group and those for the unresponsive soils in another group (Olson, 1946; Ensminger and Larson, 1944; Lawton *et al.*, 1947; Hockensmith *et al.*, 1933). It is the hope and expectation, of course, that the soil test results for the responsive soils will all fall *below* some critical value and those for the unresponsive soils will fall *above* this value. Because of experimental error and other causes, this is seldom if ever realized. A perusal of the published data on soil test correlation shows that medium to high testing soils seldom give a crop response, whereas low testing soils may fail to give a crop response. This is well illustrated by the data of Hockensmith *et al.* (1933) and Long (1947). Data obtained by Ensminger and Larson (1944) and Bingham (1949) are shown in Tables V and VI, respectively. The data by Bing-

TABLE V

PHOSPHORUS SOLUBLE IN CARBON DIOXIDE-SATURATED WATER IN RELATION TO CROP RESPONSE TO PHOSPHATE FERTILIZATION[a]

Response categories	*No. of samples*	*Mean value of soluble P_2O_5, pounds per acre*
High	20	9.83
Medium	25	11.75
Low	21	19.50
None	28	21.50
High + medium	45	10.93
Low + none	49	20.68

[a] Ensminger and Larson (1944).

TABLE VI

WATER-SOLUBLE PHOSPHORUS IN RELATION TO RESPONSE OF CROPS TO PHOSPHORUS IN 108 FIELD TRIALS IN CALIFORNIA[a]

PO_4 extracted, p.p.m. (solution basis)	*No. of field trials*	*Per cent of soils responding to fertilization*
0–0.2	54	85
0.21–0.3	11	82
0.31–0.4	7	100
0.41–0.5	6	16
0.51–1.0	9	13
Over 1.0	21	5

[a] Bingham (1949).

ham serve to illustrate that, whereas little response is anticipated above a given phosphorus level, 0.4 p.p.m. in this instance, apparent response may be obtained at a considerably higher level. Hence, in calibration studies the investigators are concerned with probabilities. Smith (1948), in thirty field trials, found that most crops on high lime soils in southern Idaho do not respond to phosphate when the soil contains more than 25 pounds of P_2O_5, as determined by the CO_2 method.

A number of reasons why soils testing low in phosphorus fail to respond can be given in addition to the one that the soil test itself might not be reliable. Unfavorable growth conditions, such as a deficiency of available nitrogen, is an important reason for such discrepancies. For example, Long (unpublished data) found no response of corn to phosphorus or potassium at the West Tennessee Experiment Station when 16 pounds of nitrogen per acre was applied. When the nitrogen application was raised to 48 pounds, a significant response to phosphorus and potassium resulted. Lynd *et al.* (1949) in a rotation experiment on Brookston soil found that the nitrogen supply was the important factor in governing yields of corn rather than the supply of phosphorus. Olson (1946) reported that supplies of sulfur and lime were affecting calibration of the phosphorus test.

Another important reason for unsatisfactory correlation of soil test results and crop response is the inclusion of data from two or more distinctly different "populations." Grouping of data according to important differences in soil properties may help to separate unlike populations. Burd and Murphy (1939) reported that they could explain many of the so-called exceptions in correlation by taking into account such soil properties as the buffer capacity, the phosphate absorption capacity, and the degree of saturation. Seatz (unpublished data) found that cer-

lain Tennessee soils, testing low in available phosphate in the surface layer but not responding to phosphorus fertilization, had subsoils with a medium to high level of available phosphate. He suggested that the subsoil phosphate level explained the lack of crop response of these low-testing soils.

Improvements in the interpretation of the tests are possible when such properties as pH, soil texture, fixing power of soils for phosphorus, and type of colloid are considered. In the lactate method of Egner, Riehm (1940) proposes different limiting values for the need of phosphorus both with regard to pH and to texture of soils. Prince *et al.* (1948) and Beater (1949) consider the phosphorus fixation capacity as an important factor to be included in the interpretation of the tests. Van der Paauw *et al.* (1951) found that, by the citric acid method, the correlation between the P value and crop response varied with the origin of the soil.

In addition to other means of identifying the type of colloid present, the determination of the ratio of cation exchange capacity to anion exchange capacity (C/A ratio), as proposed by Mehlich (1948), has been found useful. The range of C/A ratios of soils from various sections of the United States is shown in Table VII. This method has been employed

TABLE VII

CATION EXCHANGE-ANION EXCHANGE RATIOS OF SOILS FROM VARIOUS PARTS OF THE UNITED STATES

Soil type and state	*C/A ratio*	*Soil type and state*	*C/A ratio*
Leon fine sand, Fla.	6.7	Lufkin silt loam, Tex.	1.8
Colby silt loam, Kan.	4.7	Putnam silt loam, Mo.	1.8
Holdredge silt loam, Neb.	3.9	Sassafras silt loam, N. J.	1.7
Harpster clay loam, Iowa	3.0	White Store clay loam, N. C.	1.7
Brookston silty clay, Ind.	2.8	Craven very fine sandy loam, N. C.	1.6
Norfolk sand, N. C.	2.5	Georgeville clay loam, N. C.	0.7
Amsterdam silt loam, Mont.	2.3	Cecil loam (Wake Co.), N. C.	0.7
Miami silt loam, Wis.	1.9	Cecil clay loam (Rutherford Co.) N. C.	0.4
Orangeburg fine sandy loam, Miss.	1.9	Fannin sandy loam, N. C.	0.4
Agawam fine sandy loam, Mass.	1.8		
Kirkland silty loam, Okla.	1.8		

in a greenhouse experiment with cotton grown on soils of varying C/A ratios. The amounts of phosphorus extracted with the 0.05 *N* HCl plus 0.025 *N* H_2SO_4 mixture corresponding to optimum plant growth of soils of varying C/A ratios are presented in Fig. 6. The results show

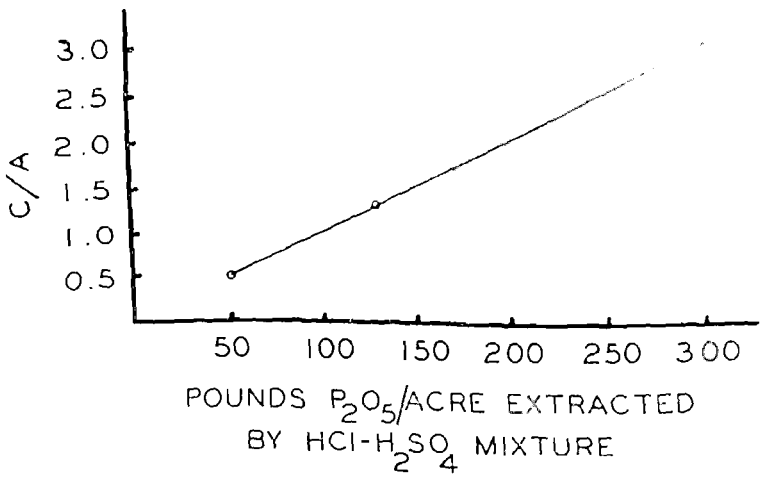


FIG. 6. Relationship between amounts of phosphorus extracted by HCl and H_2SO_4 at optimum growth of cotton on soils of varying C/A ratios.

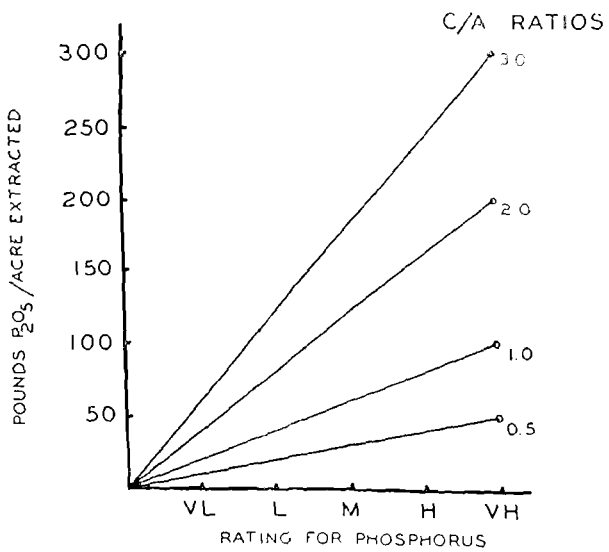


FIG. 7. Relationship between pounds of P_2O_5 extracted, C/A ratios, and soil ratings for phosphorus.

optimum growth to be at an increasingly higher level of phosphorus with increasing C/A ratio. Hence, if the method is to be used successfully, different levels for phosphorus sufficiency must be established for different soils. An illustration of this relationship is presented in Fig. 7. The accuracy of these relationships, particularly with response to different plant species, is yet to be established.

2. *Evaluation of Different Soil-Testing Procedures*

It seems safe to assume that practically all the soil-testing methods proposed have seemed satisfactory under a limited range of conditions; that is to say, for some certain crop or limited group of crops growing on soils which have a relatively narrow range in those properties affecting plant growth. On the other hand, it is fair to say that none of the tests has been entirely satisfactory when applied to a wide range of soil and crop conditions. An attempt will be made to evaluate some of the soil-testing procedures as to their general suitability for certain purposes. The evaluation will be based on data which measure the ability of the soil-testing procedure to predict crop response to phosphate fertilization.

a. Extraction Methods. Most of the soil-testing laboratories which handle large numbers of samples from farmers use one of the chemical methods. This is because chemical determinations can be made rapidly, particularly in contrast to the methods involving plants or microorganisms. Present-day instrumentation is such that chemical methods, when used in modern laboratories, can be accurate as well as rapid. The chief problem then is to select a chemical method which will give as good a correlation as possible with crop response for the soils in a given region.

Hockensmith *et al.* (1933) compared several soil-testing procedures on calcareous soils of known crop response in Colorado. They found the best correlation with the potassium carbonate extraction procedure. Ensminger and Larson (1944) found good correlation with crop response on the alkaline soils of Idaho, using CO_2 extraction for available phosphorus. On alkaline soils, the use of an Na or K ion exchanger should, on theoretical grounds, prove likewise fairly successful.

Anderson and Noble (1937) compared a number of soil-testing procedures on a group of surface soil samples that ranged from neutral to strongly acid in reaction. For the majority of the acid extraction procedures, the correlation among the tests was reasonably satisfactory. The alkaline extraction procedure varied considerably from the acid extractants from soil to soil. Even though crop response to phosphate was not known, their study suggests that several of these tests would be equally satisfactory for predicting crop response to phosphate fertilization once they had been calibrated properly for the soils studied.

Rubins and Dean (1946) compared a group of soil tests on certain soils of the Northeast of known crop response to phosphate. There was a high correlation among the predictive values of all but two of the tests. They suggest that the five tests which correlated well with each

other could have been used with equal satisfaction for predicting crop response to fertilization on the soils studied. They also point out, however, that, had they used a group of soils having a greater range in properties, the correlation might have been less satisfactory.

The Soil Test Work Group (1951) called attention to the great diversity of soil-testing methods employed throughout the country and suggested the desirability of greater uniformity in methods, particularly in adjacent areas having similar soil and crop conditions. Apparently, the selection of a soil-testing procedure by a laboratory or a state has been rather arbitrary in some instances.

b. Biological Methods. Methods involving plants require a relatively long time and special precautions for reliable results. For this reason, they are expensive to carry out and are suited only to special research programs. Relatively few data are available to compare the methods involving plants with other soil-testing procedures under American conditions. One of the few studies published is that by Rubins and Dean (1946). They found that the Neubauer method was less satisfactory in predicting crop response to fertilization on the soils they studied than were several of the chemical methods.

A nation-wide group of uniform phosphorus experiments was set up in 1951 cooperatively by several of the state experiment stations and the United States Department of Agriculture. Samples from the test areas (75 samples) were sent to Beltsville for determination of the *A* value of Fried and Dean (1952) in the greenhouse and for laboratory determinations of available phosphorus by several testing methods. The results of these experiments have been recently summarized. The preliminary report indicated rather good correlation between *A* values and certain of the chemical soil tests. Methods specifically designed to measure phosphorus gave higher correlation with *A* values than did the methods in which several nutrients were determined in the same extract. The reliability of certain methods was related to the type of colloid as measured by C/A ratio. This work is planned for continuation. Even though determination of the *A* value is essentially a research technique and is not adapted to routine soil testing, it promises to be of great help in providing a better measure and more complete understanding of the availability of phosphorus in the soil. McAuliffe *et al.* (1951), in a residual phosphorus study using radiophosphorus, found an inverse relation between the percentage of phosphorus in oats derived from the fertilizer and the values for available phosphorus obtained by soil tests.

Microbiological procedures are intermediate between the chemical methods and those utilizing higher plants as to the time and work in-

volved. In general, the microbiological procedures as such are too time-consuming at present to be well suited for general use in soil-testing laboratories. Thus, they represent essentially a method for special research studies.

Hockensmith *et al.* (1933) found that the *Azotobacter* method was less satisfactory than the potassium carbonate method for predicting crop response on calcareous soils in Colorado. Long (1947) found that there was little or no difference between the microbiological soil test (*Cunninghamella*) and the modified Bray test in predicting crop response to phosphorus on the moderately acid soils of Tennessee. Some unpublished work of Burg and Sherbakoff in Tennessee suggests that one of the difficulties of the microbiological tests may be variable competition with other soil microorganisms from soil to soil. One way to eliminate the undesirable effect of so-called "microbiologic weeds" would be sterilization of the sample before inoculation with the testing organism. Burg and Sherbakoff (unpublished) obtained more satisfactory growth of the test organism and better correlation with field results when samples were subjected to preliminary sterilization. In a comparison of testing methods on 122 soils reported by Mitscherlich (1936), the *Cunninghamella* method compared favorably with the Neubauer and lactate methods (Table VIII).

TABLE VIII

COMPARISON OF MITSCHERLICH, NEUBAUER, LACTATE, AND CUNNINGHAMELLA METHODS FOR PHOSPHORUS[a]

Phosphorus response group according to Mitscherlich	*No. of soils*	*No. of soil test values falling in same group according to:*		
		Neubauer	*Lactate*	*Cunninghamella*
High response	26	18	17	17
Moderate response	38	28	26	29
Slight response	39	32	37	36
No response	19	15	15	15

[a] Mitscherlich (1936).

3. *Future Work in Evaluation Needed*

Apparently, nearly all workers who have published on the general problem of soil tests for available phosphorus agree as to the importance of correlation with crop response data (Morgan, 1941; Jenny *et al.*, 1950; Bray, 1948; and Merkle, 1940). Nevertheless, much of the work that has been published on the correlation of soil test data and crop response seems to have been derived from experiments which

were set up for other purposes (Bray, 1944; Long, 1947; Hockensmith *et al.*, 1933), rather than from experiments designed especially for the study of such correlations.

It would be desirable that, in the future, experiments be specifically designed and initiated to determine the correlation between soil test and crop response. Some standardization of soil-testing procedures from state to state, as suggested by the Soil Test Work Group (1951), should expedite correlation studies by permitting a regional or subregional approach to the problem. This would be in contrast to the present situation, where nearly every state is using a different soil-testing procedure and attempting to make its own correlations.

Attention should be given also to the phosphate availability and supply in the subsoil. Frequently, the vegetative response of a crop to phosphorus in the early season fails to be registered in terms of final yield differences (Stanford and Nelson, 1949; Nelson *et al.*, 1949). This has been due to dilution effects, in that, with progressing development, a larger proportion of roots draw more from the unfertilized areas of the soil. Unpublished data by N. S. Hall *et al.* show that, when P^{32} was uniformly distributed throughout the soil, tobacco removed 20 per cent of the P^{32} from the surface and 80 per cent from the soil below 8 inches. Cotton, on the other hand, removed 60 to 70 per cent of the P^{32} from the surface zone and only 30 to 40 per cent from the lower depths.

The release of available phosphorus during the season by organic matter decomposition is another factor which may lead to unsatisfactory correlation with soil test data. Several states are giving attention to this problem, but no entirely satisfactory solution is in immediate sight. The problem becomes especially important when calibrations are attempted with soils showing considerable range in total and readily decomposable organic matter. For soils which are relatively uniform in their organic content and composition, this factor apparently is of less importance. Again, organic matter relationships can often be predicted on the basis of soil series or soil region.

The application of rock phosphate to soils leads to rather high test results with those methods which call for moderately to strongly acid extractants, even though certain crops, such as wheat and tobacco, may give good response to phosphate fertilization on such soils. In Illinois, Bray (1944) developed a 0.025 *N* HCl + 0.03 *N* NH_4F mixture which dissolves only small portions of the rock phosphate. A similar problem appears to exist on certain soils which have a naturally high phosphate content, such as is the case in the Bluegrass area of Tennessee and Kentucky. The moderately to strongly acid extractants, when used on such soils, usually give fictitiously high phosphate estimates that are

frequently not in agreement with crop response. Further study of this problem is particularly important in the local areas of high phosphate soils, as well as in those areas where rock phosphate has been generally used or is coming into more general usage.

IV. Use of Soil Tests

In spite of the many limitations of soil-testing techniques, it must be admitted that considerable advancement has been made, based primarily on increased knowledge of soil chemistry.

A recent report of the Soil Test Work Group (1951) revealed that virtually all states had a soil-testing service. One and a quarter million samples are reported to be run annually in the United States. Phosphorus was determined in each of these soil-testing laboratories. In addition, there are many commercial soil-testing laboratories in the United States, almost all of which determine phosphorus. Soil phosphorus has also been determined on an extensive basis in many soil-testing programs in Europe for many years.

Soil testing on a service basis means handling relatively large numbers of samples. It is important that labor-saving equipment be used in such instances in order that the volume of work can be handled rapidly yet accurately. Drawings of certain of the equipment as well as a listing of other items of equipment are given in the report of the Soil Test Work Group (1951). Such equipment has been used in routine tests for phosphorus in a few laboratories such as described by Miles and Reed (1948), Hester (1948), and Wormley (1951). Many laboratories are rapidly adopting this type of special equipment.

In such schemes, the soil is measured out by volume with a scoop into flasks assembled in extraction racks holding 12 flasks. The desired quantity of extraction solution can be added at one time to all flasks in the rack from specially built dispensers and then 36 samples shaken at one time. Filtering of 12 samples at a time is accomplished. The use of a reagent which is so made up that only one addition is necessary to develop the color for the phosphorus determination, and which can be added by electrically powered automatic pipettes dispensing 1 to 3 ml. with each stroke, speeds up the analyses considerably. The automatic balancing type of photometer to determine color intensity is most rapid. Single determinations are made on each sample, but one check sample is included in each set of 12, for control.

The use of such a scheme as described above permits analyzing large numbers of samples accurately but relatively economically. This means that many growers can take advantage of the information obtained from analyses for phosphorus on their fields.

1. Reporting Results—Actual Values versus Symbols

Some laboratories report the results of soil tests for phosphorus in terms of pounds of P_2O_5 per acre or parts per million of P. Other laboratories report in terms of rating symbols such as VL (very low), M (medium), H (high), and VH (very high). In general, the significance of these symbols has not been agreed upon among states.

There are advantages for each type of procedure. Reporting in terms of actual amounts has some advantage over the use of symbols because

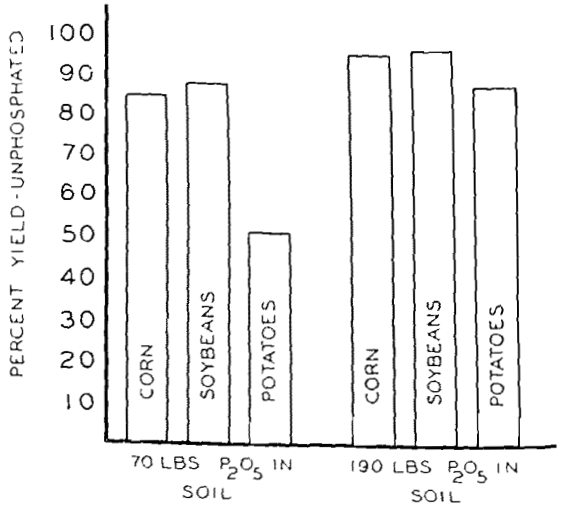


FIG. 8. Response of corn, soybeans, and potatoes to phosphorus (Krantz *et al.*, 1949).

crops vary in their requirements. A soil which is medium in phosphorus for one crop might not be medium for another crop because of differences in extent of root system, rapidity of growth, and other characteristics of growth. Several examples might be cited.

In an experiment on a Bladen silt loam containing 70 pounds of P_2O_5 per acre (Truog), Krantz *et al.* (1949) found that corn and soybeans responded little to an application of 100 pounds of P_2O_5, whereas the yield of Irish potatoes was more than doubled (Fig. 8). This soil would have been classified as M. On another Bladen silt loam considered H in phosphorus, corn and soybeans did not respond to phosphorus but Irish potatoes did. In an experiment reported by Krantz *et al.* (1949), cotton and corn were grown on a soil containing 58 pounds of P_2O_5 per acre (M). Corn gave no yield response to 50 pounds of P_2O_5 in the fertilizer, but yields of cotton were increased 70 per cent. These crop

differences must then be taken into consideration in making recommendations for phosphorus based on soil tests.

The pounds of P or P_2O_5 reported will, of course, vary with the extractant and the soil:solution ratio. Bingham (1949), working with California soils and using a water extractant with a soil:water ratio of 1:10, concluded that on soils where the filtrates contained less than 0.4 p.p.m. of P the crops would be likely to respond to applications of phosphorus. A response was not expected when the filtrate contained above 0.5 p.p.m. Spurway (1944), using a weak acetic acid extractant and a somewhat narrower soil:solution ratio, had a considerably higher range —up to 40 pounds of P per acre or above. On the other hand, Bray (1948) has used a relatively strong extracting solution of 0.1 *N* HCl and 0.03 *N* ammonium fluoride. The range of his method extends to over 92 pounds of P per acre.

The system of rating symbols has some obvious advantages. In the first place, five ranges of phosphorus level are perhaps detailed enough in evaluating the phosphorus needs of the farmers' fields. The effects of time and method of application, source of phosphorus, season, and other growth factors are such that extreme detail in reporting is not needed. If more exact records are needed, the photometer readings or values for actual amounts can be retained in the files along with the rating symbols. The differences among crops in phosphorus requirement may be compensated for by adjustment in the rating symbols. It will also be necessary to adjust for differences among soils (see Section III.1.b. and Figs. 6 and 7).

Another advantage attributed to the use of rating symbols has to do with the education of the farmer as to the meaning of the values reported for phosphorus. The farmer has some basis for knowing what VL or L or H and VH means in terms of the general condition of his bank account, the expected rainfall, and the fertility level of his soil. He would need considerably more education to know what 70 pounds of P per acre connotes in terms of the phosphorus needs on his soil. In addition, the needs of his soil in terms of pounds of P_2O_5 per acre cannot be determined by looking at the pounds of P per acre in the soil and simply adding the given amount to bring the soil up to optimum phosphorus fertility. An interpretation of the results is needed.

2. *Phosphorus Fertilization Recommendations Based on Soil Tests*

The general recommendations of the Experiment Station and the Extension Service are of necessity based on average conditions. Through the use of soil tests the amounts of phosphorus recommended are adjusted up or down depending on the results of the analysis. In attempt-

ing to make these adjustments it is essential that the soil test results be calibrated against results obtained in fertility experiments conducted on soils of varying phosphorus level.

The farmer usually wants to know two things about his soil: (a) how much it will respond to fertilizer, phosphorus in this instance, and (b) how much fertilizer will be required to produce this response. Soil test results are generally used to recommend phosphorus to help answer (b). Bray (1948), in studies of Illinois soils, however, predicts the percentage yields on soils by determining the available phosphorus and potassium in the soils. Attoe and Truog (1949) developed an equation through which the yields of alfalfa and clover hay could be predicted as follows:

Tons hay per acre $= a$ log lb. available P $+ b$ log lb. exchangeable K $+ c$

The values of a, b and c were found to vary with weather conditions and type of soil. It is recognized, however, that poor crop yields are not always due to nutrient deficiencies. Variety, cultural practices, seasonal conditions, insects, and diseases all enter the picture.

3. *Recommendations on Soils Low in Phosphorus*

There are two general types of approach when a soil is low in phosphorus. One approach is to apply considerably more than maintenance amounts for a few years and then to retest the soil to determine if the treatment has brought the supply of phosphorus to an adequate level. If the supply of phosphorus is satisfactory, maintenance amounts can be added to take care of crop removal, fixation, and losses by erosion and leaching.

The other approach is to add small amounts of fertilizer and give careful attention to placement. This refers to the time of application in the rotation and to the placement in the soil with respect to the plant roots. This approach demands well-calibrated tests, and even then there is more opportunity for error through recommending inadequate amounts.

Bray (1944) and Bray and Melsted (1948) are applying the former approach to Illinois soils. They emphasize that soil tests help to measure the balance between all the additions and all the losses. They stress the need for continued soil tests at six- to eight-year intervals in order to use added fertilizer efficiently. This method is, of course, much easier to follow when the farmer's economic condition is good, as then he is more readily convinced of the importance of building the fertility of his soil. When the farmer's economic condition is poor, he may want to revert to the "hand-to-mouth" procedure. Bray (1944) recognizes this in his minimum and maximum recommendations.

a. Rotation versus Individual Crops. There has been a marked tendency to make recommendations for specific crops. However, many recommendations are now being made on a rotation basis with particular emphasis on the placement of the phosphorus and other fertilizer in the rotation (Soil Test Work Group, 1951). This trend has been particularly evident in the North Central and Northeastern States. In the Southern region rotational systems are not quite so well established as yet.

The residual effect of past crop fertilization on the phosphorus level of the soil was recently pointed out by Welch and Nelson (1951). On soils on which tobacco and cotton were planted, approximately 80 per cent tested high or very high in phosphorus. Tobacco and cotton receive about 100 and 50 pounds of P_2O_5, respectively, each time they are grown. On the other hand, peanuts usually receive no phosphorus fertilization, yet 80 per cent of the soils were high or very high in phosphorus. Peanuts, however, are usually grown in rotation with cotton. Such facts as these are important in deciding on the fertilization.

b. Grades and Materials. In some instances, soil-testing programs are hampered by unavailability of suitable grades of fertilizer to meet varying conditions. In the South mixed fertilizers are used universally and there is less emphasis on materials. Taking corn needs, for example, if grades of the ratios 1-1-1, 1-2-1, 1-2-2, and 1-1-2 are available, most conditions can be met. Of course, nitrogen materials are applied as side-dressing.

Phosphorus materials permit considerable flexibility and, in the above instance, soils very low in phosphorus might be supplemented with phosphorus materials. For Ladino-grass pastures Collins (1952) emphasizes the need for superphosphate in addition to 2–12–12 when the soils are low in phosphorus.

4. Information through Summaries

It is recognized that the primary purpose of soil tests is to give the individual farmer dependable information as to the fertility status of each of his fields. However, a summary of soil-testing data on a state, on a county, or on a type-of-farming or soil association basis shows general fertility levels. This is of value to educational agencies and to lime, fertilizer, and related industries in promoting their respective programs.

Several such summaries of soil test data have been made, but most of these summaries were only in mimeographed form and little attempt was made to make a thorough interpretation of the information. Three such summaries have been made of North Carolina soil test data since 1945 (Miles, 1946; Parker *et al.*, 1951; Welch and Nelson, 1951; Nelson

and Welch, 1952) and two of Tennessee data (Parker *et al.*, 1951, and Bishop, 1951).

The data from North Carolina by Welch and Nelson (1951) show that the extractable soil phosphorus level varies greatly among counties and that the counties having the highest phosphorus levels are in the Coastal Plain (Fig. 9). A comparison of fertilizer usage and phosphorus level reveals the close relationship between fertilizer usage and phosphorus level in the soil. The fertilizer usage and phosphorus levels can be generally related to the distribution of the acreage of tobacco and cotton.

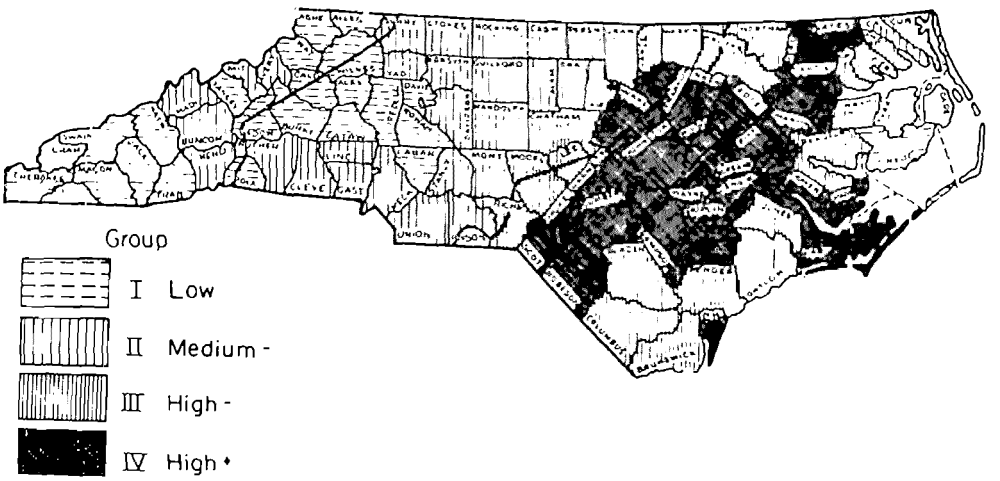


FIG. 9. Available phosphorus in soil of North Carolina counties (Welch and Nelson, 1951).

In Table IX the soil tests for phosphorus are summarized with respect to the crop to be grown. This tabular information is quite valuable in a number of respects. Mehring and Parks (1949) point out that North Carolina farmers applied over five times as much phosphorus as was contained in harvested crops. The data in Table IX emphasizes the need for redistribution of the fertilizer phosphorus in North Carolina.

A summary of Tennessee soil test data by Parker *et al.* (1951) showed that the phosphorus level in the soil was related to soil associations. This was particularly striking in Central Tennessee.

a. Special Uses of Soil Test Summaries. The local agricultural leaders can utilize summaries to point out specific fertility problems on the crops in his county. The data help to establish the general need for special fertilizer treatments.

Agronomy extension specialists can use the summaries to encourage certain fertilization practices. For example, in certain areas the fields going into Ladino-grass may be very low in phosphorus and the specialists can emphasize the need for extra phosphorus at planting. They can also use the information to stimulate interest in soil tests.

TABLE IX

PHOSPHORUS LEVEL AS RELATED TO CROP TO BE GROWN[a]

Crop to be grown	*No. of samples tested*	*Percentage of samples testing*				
		Very low	*Low*	*Medium*	*High*	*Very high*
Tobacco (flue-cured)	11,868	3	8	7	18	64
Tobacco (Burley)	219	24	21	20	12	23
Cotton	2,165	8	12	9	17	54
Corn	7,351	18	22	11	16	33
Peanuts	1,660	1	7	11	22	59
Soybeans	443	8	21	19	19	33
Ladino-grass	4,274	32	32	12	12	12
Other pastures	648	45	31	8	8	8
Alfalfa	1,693	33	33	11	11	12
Irish potatoes	291	6	7	3	14	70
Sweet potatoes	83	5	12	10	14	59
Other truck crops	805	5	13	9	15	58

[a] Welch and Nelson (1951).

Soil test summaries are useful to industrial agronomists in that they help in predicting the fertilizer analyses (or grades) which will be most frequently required and recommended in general areas. This will make for more efficient use of phosphorus.

Experiment Station workers should be interested in such summaries because they help to indicate where soil fertility efforts should be concentrated. Soil test summaries are useful to the station workers in establishing new grades. An example of this in North Carolina was the adding of 4–8–10 to the grade list as a general substitute for 3–9–6, the old established tobacco fertilizer.

REFERENCES

ANDERSON, M. S., and NOBLE, W. M. 1937. Comparison of various chemical quick tests on different soils. *U.S. Dept. Agr. Misc. Publ.* **259.**

ARNOLD, C. V., and SCHMIDT, W. A. 1951. Soil tests as a measure of phosphorus available to tomatoes on heavy soils. *Soil Sci.* **71**: 105–115.

ATTOE, O. J., and TRUOG, E. 1949. Correlation of yield and quality of alfalfa and clover hay with levels of available phosphorus and potassium. *Soil Sci. Soc. Amer. Proc.* **14**: 249–253.

BATES, R. G., and ACREE, S. F. 1943. H values of certain phosphate–chloride mixtures, and the second dissociation constant of phosphoric acid from 0° to 60°C. *J. Research Natl. Bur. Standards* **30**: 129–155.

BAVER, L. D., and BRUNER, F. H. 1939. Rapid soil tests for estimating the fertility needs of Missouri soils. *Missouri Agr. Expt. Sta. Bull.* **404**.

BEATER, B. E. 1949. A rapid method for obtaining readily soluble phosphates and phosphate fixation in soils. *Plant and Soil* **1**: 215–220.

BENECKE, W., and SÖDING, H. 1928. Beiträge zum Ausbau der mikrobiologischen Bodenanalyse. *Z. Pflanzenernähr. u. Düngung* **A10**: 129–159.

BINGHAM, F. T. 1949. Soil test for phosphate. *California Agr.* **3**, No. 8, pp. 11, 14.

BISHOP, W. D. 1951. Soil testing summary. *Tennessee Agr. Expt. Spec. Circ.* **375**.

BLENKINSOP, A. 1938. Soil studies for advisory purposes. *Agr. Progress* **15**: 184–193.

BONDORFF, K. A., and DAMSGAARD-SORENSEN, P. 1942. The phosphoric acid content of soils. III. A comparison of different chemical methods of determining the available phosphate in soil. *Tidsskr. Planteavl.* **46**: 377–425.

BRAY, R. H. 1937. New concepts in the chemistry of soil fertility. *Soil Sci. Soc. Amer. Proc.* **2**: 175–179.

BRAY, R. H. 1944. Soil test interpretation and fertilizer use. *Illinois Agr. Expt. Sta., Agron. Dept. Pamphlet Ag.* 1198b.

BRAY, R. H., and MELSTED, S. W. 1948. Maintenance requirements for fertile soils. *Illinois Agr. Expt. Sta., Agron. Dept. Pamphlet Ag.* 1359.

BRAY, R. H. 1948. Correlation of soil tests with the crop response to added fertilizers and with fertilizer requirement. Diagnostic Techniques for Soils and Crops, Chapter II, pp. 53–86. American Potash Institute. Washington, D. C.

BRIND, W. D. 1950. Recent work on the chemical determination of readily soluble phosphorus in soil. *Soils and Fertilizers* **13**: 235–239, 315–320.

BURD, J. S., and MURPHY, H. F. 1939. The use of chemical data in the prognosis of phosphate deficiency in soils. *Hilgardia* **12**: 323–340.

BUTKEWITSCH, W. 1909. Die Kultur des Schimmelpilzes *Aspergillus niger*, als Mittel zur Bodenuntersuchung. *Zhur. Opyt. Agron.* **10**: 136–141.

COLEMAN, N. T., JACKSON, M. L., and MEHLICH, A. 1949. Mineral composition of the clay fraction. II. Of several Coastal Plain, Piedmont and Mountain soils of North Carolina. *Soil Sci. Soc. Amer. Proc.* **14**: 81–85.

COLLINS, E. R. 1952. North Carolina fertilizer recommendations for field crops. North Carolina Agricultural Extension Service.

COOKE, G. W. 1951. Fixation of phosphate during the acid extraction of soils. *J. Soil Sci.* **2**: 254–262.

DAHLBERG, H. W., and BROWN, R. J. 1932. A study of the Neubauer and Winogradsky (*Azotobacter*) methods as compared with a chemical method for the determination of phosphorus deficiency in western soils. *J. Am. Soc. Agron.* **24**: 460–468.

DAS, S. 1930. An improved method for the determination of available phosphoric acid in soils. *Soil Sci.* **30**: 33–49.

DAUBENY, G. 1845. Memoir on the rotation of crops and the quantity of inorganic matter abstracted from soil by various plants under different circumstances. *Royal Soc. (London) Phil. Trans.* 179–252.

DIRKS, B., and SCHEFFER F. 1928. Rapid method for the determination of the phosphorus requirements of soils. *Landwirtsch Jahrb.* **67**: 779.

EGNER, H. 1941. The Egner lactate method for phosphate determination. *Am. Fertilizer* **94**: 5–7, 22, 24, 26.

ENSMINGER, L. E., and LARSON, H. W. E. 1944. Carbonic acid soluble phosphorus and lime content of Idaho soils in relation to crop response to phosphate fertilization. *Soil Sci.* **58**: 253–258.

FORSEE, W. T. 1950. The place of soil and tissue testing in evaluating fertility levels under Everglades conditions. *Soil Sci. Soc. Amer. Proc.* **15**: 297–299.

FRAPS, G. S. 1909. Active phosphoric acid and its relation to the needs of the soil for phosphoric acid in pot experiments. *Texas Agr. Expt. Sta. Bull.* **126**.

FRIED, M., and DEAN, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

GHANI, M. Q. 1943. The use of 8-hydroxyquinoline as a means of blocking active iron and aluminum in the determination of available phosphoric acid of soils by dilute acid extractions. *Indian J. Agr. Sci.* **13**: 562–565.

GOODWIN, J. B. 1935. The use of electrodialysis for estimating phosphate availability in calcarerous soils. *Colorado Agr. Expt. Sta. Tech. Bull.* **12**: 1–32.

HENDA, A. VAN DEN. 1950. The value of chemical methods in studying the phosphoric acid requirement of Belgian soils. *Trans. 4th Internat. Congr. Soil Sci.* **1**: 218–221.

HESTER, J. B. 1948. Operation of an industrial service laboratory for analyzing soil and plant samples. Diagnosis Techniques for Soils and Crops, Chapter IV, pp. 105–135. American Potash Institute, Washington, D. C.

HIBBARD, P. L. 1931. Chemical methods for estimating the availability of soil phosphorus. *Soil Sci.* **31**: 437–467.

HOCKENSMITH, R. D., GARDNER, R., and GOODWIN, J. 1933. Comparison of methods for estimating available phosphorus in alkaline calcareous soils. *Colorado Agr. Expt. Sta. Tech. Bull.* **2**.

JENNY, H., VLAMIS, J., MARTIN, W. E. 1950. Greenhouse assay of fertility of California soils. *Hilgardia* **20**: 1–8.

JONES, G. H. G. 1949. Proceedings of the First Commonwealth Conference on Tropical and Subtropical Soils. Discussion on soil fertility problems. *Commonwealth Bur. Soil Sci. Tech. Commun.* **46**: 180.

KERR, H. W., and VON STIEGLITZ, C. R. 1938. The laboratory determination of soil fertility. *Queensland Dept. Agr. Brisbane, Tech. Commun.* **9**: 179–203.

KRANTZ, B. A., NELSON, W. L., and BURKHART, L. F. 1948. Plant tissue tests as a tool in agronomic research. Diagnostic Techniques for Soils and Crops. Chapter V, pp. 137–155. American Potash Institute, Washington, D. C.

KRANTZ, B A., NELSON, W. L., WELCH, C. D., and HALL, N. S. 1949. A comparison of phosphorus utilization by crops. *Soil Sci.* **68**: 171–177.

KURTZ, T., DETURK, E. E., and BRAY, R. H. 1946. Phosphate adsorption by Illinois soils. *Soil Sci.* **61**: 111–124.

LAATSCH, W. 1941. Die Festlegung der Phosphorsäure an Tone. *Bodenkunde u. Pflanzenernähr.* **23**: 17–31.

LAWTON, K., ROBERTSON, L. S., COOK, R. L., and ROAD, P. J. 1947. A study of correlation between rapid soil tests and response of legume hay to phosphorus and potassium fertilization on some Michigan soils. *Soil Sci. Soc. Amer. Proc.* **12**: 353–358.

LEMMERMAN, O., and FRESENIUS, L. 1934. Methoden für die Untersuchung des Bodens. II. Teil Verlag Chemie, Berlin.

LONG, O. H. 1947. A comparison of two soil test methods as correlated with wheat and cotton response to fertilizers. *Soil Sci. Soc. Amer. Proc.* **12**: 255–261.

LONG, O. H. 1951. Correlation of soil tests for available phosphorus and potassium

with crop yield responses to fertilization. M.S. thesis. University of Tennessee, Knoxville, Tennessee.

LUNT, H. A., SWANSON, C. L. W., and JACOBSON, H. G. M. 1950. The Morgan soil testing system. *Connecticut Agr. Expt. Sta. Bull.* **541**: 1–60.

LYND, J. Q., TURK, L. M., and COOK, R. L. 1949. Application of soil tests, tissue tests and foliar analyses to field experiments. *Soil Sci. Soc. Amer. Proc.* **14**: 236–241.

MCAULIFFE, C., STANFORD, G., and BRADFIELD, R. 1951. Residual effects of phosphorus in soil at different pH levels as measured by yield and phosphorus uptake of oats. *Soil Sci.* **72**: 171–177.

MCGEORGE, W. T. 1939. Studies on plant food availability in alkaline-calcareous soils: Seedling tests and soil analyses. *Arizona Agr. Expt. Sta. Tech. Bull.* **82**: 295–331.

MATTSON, S., ALVSAKER, E., KOUTLER-ANDERSON, E., BARKOFF, E., and VAHTRAS, K. 1950. Phosphate relationships of soil and plant. VI. The salt effect on phosphate solubility in Pedalfer soils. *Ann. Agr. Coll. Sweden* **17**: 141–160.

MEHLICH, A. 1939. Growth of *Cunninghamella blakesleeana* as influenced by forms of nitrogen and phosphorus under varying conditions. *Soil Sci.* **48**: 121–133.

MEHLICH, A. 1948. Determination of cation and anion exchange properties of soils. *Soil Sci.* **66**: 429–445.

MEHLICH, A., and COLWELL, W. E. 1943. Influence of nature of soil colloids and degree of base saturation on growth and nutrient uptake by cotton and soybeans. *Soil Soc. Soc. Amer. Proc.* **8**: 179–184.

MEHLICH, A., FRED, E. B., and TRUOG, E. 1934. The Cunninghamella plaque method of measuring available phosphorus in soil. *Soil Sci.* **38**: 445–461.

MEHRING, A. L., and PARKS, R. O. 1949. How nutrients removed from soil by harvested crops are replaced by fertilizers. *Agr. Chemicals*, Oct. and Nov.

MERKLE, F. G. 1940. Soil testing. *Pennsylvania Agr. Expt. Sta. Bull.* **398**.

MILES, I. E. 1946. Soil testing—one year summary. July 1, 1944–June 30, 1945. Soil Testing Division, North Carolina Department of Agriculture.

MILES, I. E., and REED, J. F. 1948. Operation of a state soil testing laboratory. Diagnostic Techniques for Soils and Crops, Chapter III, pp. 87–103. American Potash Institute, Washington, D. C.

MITSCHERLICH, E. A. 1930. Die Bestimmung des Düngerbedürfnisses des Bodens, 3rd ed. Paul Parey, Berlin.

MITSCHERLICH, E. A. 1936. Erster Bericht über die Arbeiten und über die Tagung der Arbeitsgemeinschaft zur Prüfung der Laboratoriumsmethode für die Bestimmung des Kali- und Phosphorsaürebedürfnisses des Bodens. Commission IV. *Proc. Internat. Soc. Soil Sci.* Königsberg.

MOOERS, C. A. 1938. An evaluation of the Neubauer and the *Cunninghamella* and *Aspergillus niger* methods for the determination of the fertilizer needs of a soil. *Soil Sci.* **46**: 211–227.

MORGAN, M. F. 1937. The Universal Soil Testing System. *Connecticut Agr. Expt. Sta. Bull.* **392**: 129–159.

MORGAN, M. F. 1941. Chemical diagnosis by the Universal Soil Testing System. *Connecticut Agr. Expt. Sta. Bull.* **450**.

MUKHERJEE, M. K. 1941. Studies on the fixation of phosphates in Indian red soils. I. Applicability of Truog's method for the determination of available phosphates. *Indian J. Agr. Sci.* **11**: 243–248.

NELSON, W. L., and HAWKINS, A. 1947. Response of Irish potatoes to phosphorus

and potassium on soils having different levels of these nutrients in Maine and North Carolina. *J. Am. Soc. Agron.* **39**: 1053–1067.

NELSON, W. L., KRANTZ, B. A., WELCH, C. D., and HALL, N. S. 1949. Utilization of phosphorus as affected by placement: II. Cotton and corn in North Carolina. *Soil Sci.* **68**: 137–144.

NELSON, W. L., and WELCH, C. D. 1952. The broad utilization of soil test information through summaries. *Trans. Intern. Soc. Soil Sci.*, Joint Meeting of Comm. II and IV, Dublin, **2**: (In press).

NEUBAUER, H., and SCHNEIDER, W. 1923. Die Nährstoffaufnahme der Keimpflanzen und ihre Anwendung auf die Bestimmung des Nährstoffgehalts der Böden. *Z. Pflanzenernähr. Düngung u. Bodenk.* **A2**: 329–362.

NIKLAS, H., POSCHENRIEDER, H., and TRISCHLER, J. 1930. Die Kultur des Schimmelpilzes *Aspergillus niger* zur biochemischen Bestimmung der Kali- und Phosphorsäurebedürftigkeit der Böden. *Ernähr. Pflanze* **26**: 97–103.

OLSON, L. S. 1946. Factors affecting the relationship between laboratory tests for soil phosphorus and crop response to applied phosphate. *Soil Sci. Soc. Amer. Proc.* **10**: 443–445.

PANTANELLI, E. 1924. Biochemical determination of the available phosphates in soil. *Actes IV conf. internat. pedologie, Rome*, **3**: 232–236.

PARKER, F. W., NELSON, W. L., WINTERS E., and MILES, I. E. 1951. The broad interpretation and application of soil information. *Agron. J.* **43**: 105–112.

PEECH, M., ALEXANDER, L. T., and DEAN, L. A. 1947. Methods of soil analysis for soil fertility investigations. *U.S. Dept. Agr. Circ.* **757**.

PEECH, M., and ENGLISH, L. 1944. Rapid micro-chemical soil tests. *Soil Sci.* **57**: 167–195.

PRINCE, A. L., TOTH, S. J., and BEAR, F. E. 1948. Phosphorus supplying powers of 20 New Jersey soils. *Soil Sci.* **65**: 297–308.

PURVIS, E. R., and HANNA, W. J. 1949. Rapid electrodialysis of soils in dilute boric acid solution. *Soil Sci.* **67**: 47–52.

REUSZER, H. W. 1936. Results from *Cunninghamella* plaque tests for available phosphorus in calcareous soils. *Soil Sci. Soc. Amer. Proc.* **1**: 197–204.

RIEHM, H. 1940. Die Berücksichtigung der Bodenart und der Reaktion bei der Phosphatmethode nach Egner. *Bodenkunde u. Pflanzenernähr.* **66/67**: 316–327.

RUBINS, E. J., and DEAN, L. A. 1946. A comparison of certain methods for determining readily soluble phosphorus in soils. *J. Am. Soc. Agron.* **38**: 820–823.

RUSSELL, E., and RUSSELL, E. W. 1950. Soil Conditions and Plant Growth, 8th ed., p. 449. Longmans, Green and Co., New York.

SEATZ, L. F. 1949. Phosphorus retention and release in soils. Ph.D. thesis, North Carolina State College, Raleigh, North Carolina.

SEKERA, F., und SCHOBER, K. 1934. Der Mikro-Düngungsversuch zur Bestimmung der Düngerwirkung von Phosphorsäure und Kali. *Die Phosphorsäure* **4**: 321–351.

SOIL TEST WORK GROUP REPORT. 1951. Soil Testing in the United States.

SMITH, F. B., BROWN, P. E., and SCHLOTS, F. E. 1932. A comparison of the Niklas and Truog methods for the determination of available phosphorus in soils. *J. Am. Soc. Agron.* **24**: 452–459.

SMITH, V. T. 1948. An evaluation of the carbon dioxide method of determining available phosphoric acid in high lime soils. *J. Am. Soc. Agron.* **40**: 1045–1046.

SPURWAY, C. H. 1944. Soil testing—a practical system of soil fertility diagnosis. *Michigan Agr. Expt. Sta. Tech. Bull.* **204** (3rd rev.).

STANBERRY, C. O. 1949. The behavior of phosphorus in an alkaline irrigated soil in Washington. *Soil Sci. Soc. Amer. Proc.* **13**: 205–212.

STANFORD, G., and NELSON, L. B. 1949. Utilization of phosphorus as affected by placement. I. Corn in Iowa. *Soil Sci.* **68**: 129–136.

STRUTHERS, P. H., and SIELING, D. H. 1950. Effect of organic anions on phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* **69**: 205–213.

TRUOG, E. 1930. The determination of the readily available phosphorus of soils. *J. Am. Soc. Agron.* **23**: 874–882.

ULRICH, A. 1948. Plant analysis—methods and interpretation of results. Diagnostic Techniques for Soils and Crops, Chapter VI, pp. 157–198. American Potash Institute, Washington, D. C.

VANDECAVEYE, S. C. 1948. Biological methods for determining nutrients in soil. Diagnostic Techniques for Soils and Crops, Chapter VII, pp. 199–230. American Potash Institute, Washington, D. C.

VAN DER PAAUW, F., DE LA LANDE CREMER, C. H. N., and RIS, J. 1951. Evaluation of soil testing on availability of phosphate on Dutch grasslands. *Versl. Landbouwk. Onderz.* **57.15.**

VON SIGMOND, A. 1929. Bestimmung von Kali and Phosphorsäure mittels *N*/100 HNO_3. II. Comm. *Internat. Soc. Soil Sci. Budapest*, **A**: 146–150.

WELCH, C. D., and NELSON, W. L. 1951. Fertility status of North Carolina soils. *North Carolina Dept. Agr. Bull.*

WILD, A. 1950a. The retention of phosphate by soil. A review. *J. Soil Sci.* **1**: 221–238.

WILD, A. 1950b. The effect of neutral salts on the retention of phosphate by clay at various pH values. *Trans. 4th Internat. Congr. Soil Sci.* **1**: 146–149.

WINOGRADSKY, S., and ZIEMIECKA, J. 1927. On a method for controlling the Azotobacter activity in soil and its importance. *Papers 1st Internat. Congr. Soil Sci.* Comm. VI, **4**: 878–882.

WORMLEY, G. W. 1951. Soil testing—basic steps in Iowa farming. *What's New in Crops and Soils*, February, p. 16.

CHAPTER VII

Comparative Efficiency of Various Phosphate Fertilizers

HOWARD T. ROGERS, R. W. PEARSON, and L. E. ENSMINGER

I. Introduction

The world production of phosphoric acid (P_2O_5), excluding ground rock phosphate, was about 5.6 million metric tons in 1950–1951 (FAO, 1951), an increase of 2.2 million tons over the previous 3-year period. Superphosphate accounted for 77 per cent of the total consumption in 1950–1951 on a world basis, and 88 per cent in North and Central America. Other sources, however, were more important than superphosphate on some continents, such as South America, where superphosphate furnished only 41 per cent of the total supply of fertilizer phosphorus.

As a result of the world shortage of sulfur, interest in sources of phosphate which are not dependent upon this critical element has been greatly stimulated. The world demand for elemental sulfur in 1950–1951 was estimated at 6.1 million tons, with a supply of only 5.6 million tons. In the face of a rapidly growing demand for plant nutrients, the sulfur shortage, which in turn limits the supply of superphosphate, might well be a serious deterrent to maximum food production unless other effective sources of phosphate fertilizer become available. Although the present outlook for supplies of sulfur is considerably improved, there are good indications now that methods of dissolving phosphate rock other than the use of sulfuric acid will gain importance in the years immediately ahead.

1. Scope

In spite of the vast amount of laboratory, greenhouse, and field testing of phosphorus carriers which has been conducted over a period of years, no attempt has been made to review the data and draw conclusions for a wide range of soils and crops. This report attempts to cover a sufficient number of investigations to get a cross section of the results obtained in the United States. Although some of the European work is cited, no claim is made of adequate coverage of the fertilizer evaluation research in other countries.

The major part of this report will be devoted to a comparison of those phosphorus carriers which are used commercially as fertilizers today or appear promising for the future. Mention will be made, however, of other chemical forms of phosphorus which currently are not in use as fertilizers and probably will never become commercial sources. Some of these compounds are present as constituents of commercial products; others are of academic interest only.

Primary emphasis in the evaluation of the various sources will be given to results of field tests in which crop yields were measured. Data from greenhouse or pot cultures will be cited, however, when field data are either unavailable or inadequate.

2. Factors Affecting Availability of Different Forms

Some of the generally recognized factors which determine the apparent relative efficiency of a particular phosphorus fertilizer are soil reaction, degree of soil phosphorus deficiency, rate of application, method of application, needs of the specific crop, and certain pedological differences. Properties of an individual carrier may affect its relative efficiency as a source of phosphorus, such as particle size, fluorine content, and possible toxic constituents. Obviously the relative importance of these and other factors varies greatly with the different carriers. For this reason a discussion of the more important factors will be developed in connection with the presentation of experimental results on the individual fertilizers.

II. Comparison of Phosphate Carriers Based on Crop Yields

1. Superphosphate

In 1843 Sir John Lawes of Rothamsted discovered that a more available source of phosphorus could be produced by treating rock phosphate with sulfuric acid. The production of superphosphate based on the process developed by Lawes was really the beginning of the phosphate industry.

For about one hundred years following the discovery of the process, ordinary superphosphate, sometimes called "acid phosphate," containing 16 to 20 per cent P_2O_5, constituted the major source of fertilizer phosphorus throughout the world and proved to be an efficient, easily manufactured material with few problems associated with its storage and application. Over the years agronomists have consistently placed superphosphate at the top of the list of phosphorus carriers with regard to plant response, and it has held this position for a wide range of soil, climatic, and crop management conditions. It was to be expected then

that superphosphate would come to be universally accepted as a standard against which other phosphorus fertilizers would be evaluated.

a. Concentrated Superphosphate as a Standard. In recent years, concentrated superphosphate (40 to 50 per cent P_2O_5) has been produced in greatly increased quantities. Mehring (1944) described the early development of the process for making concentrated superphosphate, which has been called "double," "triple," or "treble" superphosphate. It is estimated that 357,000 tons of P_2O_5 as concentrated superphosphate was produced in the United States during 1951, as compared with about 15,000 tons in 1930. The results of literally thousands of field tests, conducted under a wide variety of soil and crop conditions, have shown conclusively that concentrated superphosphate is fully as effective a source of phosphorus as is ordinary or normal superphosphate. Since ordinary superphosphate contains large amounts of sulfate introducing an additional plant growth variable in experimental work, the trend during the last decade has been toward the use of concentrated superphosphate as the standard phosphatic material in preference to ordinary superphosphate.

b. Granulation of Superphosphate. During the past twenty years there has been a gradually increasing interest in the granulation of superphosphate. The improvement in physical condition brought about by granulation, which is reflected in a greater ease of application with less loss by dusting on windy days and less caking in storage, has produced a steadily increasing demand for these materials in those areas where they have appeared on the market. It has been estimated by Hardesty and Clark (1951) that about 75 per cent of all the mixed fertilizers produced in the United Kingdom during the year 1951 was granulated. In the United States granulation has developed rapidly in some sections, particularly in the Northeast.

The agronomic value of granular versus powdered superphosphate was given a considerable amount of attention during the late 1930's, and more recently there has been a resurgence of interest in this question. Phosphorus fertilizers of relatively low solubility are known to be more effective when finely ground and mixed with the soil rather than banded. By the same token, if there is any beneficial effect of granulation on the efficiency of phosphorus fertilizers it would be expected to be most apparent in the case of soluble materials. The actual existence of such an effect, under normal fertilization practices, however, has yet to be conclusively shown. Experiments that have been conducted in the United States by Vomocil, Lawton, and Cook (1951, personal communication), Sayre (1936), Mehring *et al.* (1935), Skinner *et al.* (1941), Salter (1936), Grantham and Houghland (1937), Davis

(1937), and Hardesty and Clark (1951); in England by Russell and Garner (1941); in Scotland by Williams and Reith (1948); in France by Larsen (1951) and Garola (1951); in Sweden by Franck (1948) and Nordengren (1948); in Finland by Honkavaara (1951); and in the Soviet Union by Berezova and Fodeeva (1950), Vishinsky (1950), Lyzin (1951), and Vlasiuk (1950) show in general that the granulated materials are at least as good as the powdered form of superphosphate. This is true in spite of the fact that there has been no general agreement upon the particle size distribution of a fertilizer to be called granular. Hardesty and Clark (1951) stated that so-called granular fertilizers usually would "pass a No. 5 U. S. series sieve (4 mm openings) and be retained on a No. 18 sieve (1 mm opening)." The experiments referred to above dealt in many instances with entirely different particle size ranges, different soil and climatic conditions, and widely different rates of application. This would result in considerable variation in the results obtained. There are several exceptions to the statement that granulation has not been found to have any marked effect on the effectiveness of superphosphate. These are the results from Sweden, reported by Franck (1948) and Nordengren (1948), and from the Soviet Union, as recently reported by a number of Russian workers. During the last three years at least eighteen papers have appeared in the Russian literature dealing with the effectiveness of granulated superphosphate. The four references cited, Berezova and Fodeeva (1950), Vishinsky (1950), Lyzin (1951), Vlasiuk (1950), are typical of these reports, which claim a definite advantage for granulation in nearly every instance. In most cases the importance of including some organic material with the granulated superphosphate is stressed.

The results of recent field tests conducted by a number of state agricultural experiment stations in cooperation with the Tennessee Valley Authority testing nitric phosphates of different particle size ranges have been reported by Rogers (1951). These results indicate that the 12- to 50-mesh (U. S. series) range is about optimum for these materials. (See Section II.8.b.)

Very recently the tagged atom technique has been used in an attempt to measure the effect of the granule size of superphosphate on the uptake of phosphorus by plants. Some of the limitations of absorption data are discussed in Section III. Starostka (1951, personal communication), using wheat grown in the greenhouse, found a difference in the percentage of the plant phosphorus derived from the fertilizer as the granule size was varied. With superphosphate the granule ranges (mesh sizes) were rated as follows in decreasing order of efficiency: (1) 14 to 20; (2) 8 to 10; (3) 28 to 35; (4) 4 to 6; (5) 35. An intermediate

particle size was more efficient in furnishing phosphorus to the plants than were either very coarse or very fine particles. In general the yield data supported the plant absorption data. Vomocil, Lawton, and Cook (1951, personal communication) on the other hand, using tagged granulated and powdered superphosphate both banded and mixed in the soil, found no significant differences due to granulation in applied phosphorus uptake by beans or wheat in field tests.

The reported data suggest some advantage for granulation of superphosphate under conditions that would favor rapid conversion of the added phosphorus to less-soluble forms. Thus Franck's data indicated that granulated superphosphate had a greater immediate effect upon crop growth in broadcast application than did powdered material, whereas there was no difference in their effectiveness when the materials were drilled. Also Honkavaara (1951) reported results of a study in Finland which show that under various experimental conditions granular superphosphate had no advantage over the powdered form the first year regardless of method of application, but gave considerably better residual effects. For the most part, however, the reports to be found in the literature are not sufficiently complete in the characterization of environmental conditions to permit the formation of definite conclusions. For example, most of the experiments reported cover a period of 1 or at most 2 or 3 years, and little, if any, information is given on soil characteristics, solubility of the phosphorus in the different materials used, climatic conditions, or portion of the response curve in which measurements were made. The latter point would be of considerable importance in determining whether any existing differences could be detected using crop yield as the criterion of efficiency. Less effective forms could well furnish adequate amounts of phosphorus for maximum plant growth at high rates of application.

2. *Raw Phosphates (Ground Rock and Colloidal)*

Before the discovery of rock phosphate deposits, bones were the only known commercial source of phosphorus. Since bones supplied only a fraction of the needs, the discovery of phosphate deposits was of great interest to agricultural workers. Early work, however, showed that rock phosphate was not so good a source of phosphorus as bone meal.

Most of the rock phosphate mined is used in the production of superphosphate. Some raw phosphate, however, is used for direct application to the soil. The consumption of raw phosphates for direct application in the United States is given by regions in Table I. Most of the tonnage shown for the North Central region is used in Illinois. According to figures presented by Mehring (1948), the consumption of rock phos-

phate for direct application in the East North Central and West North Central States amounted to less than 55,000 tons in 1940. The figures in Table I show that the total consumption of the two areas amounted to 906,063 tons for the year ending June 30, 1951. For the United States as a whole, approximately 16 per cent of the P_2O_5 equivalent applied to soils was in the form of rock phosphate.

TABLE I

REGIONAL CONSUMPTION OF RAW PHOSPHATES IN THE UNITED STATES FOR DIRECT APPLICATION TO THE SOIL, 1951[a]

Region	*Tons*	*Region*	*Tons*
New England	927	East South Central	33,574
Middle Atlantic	5,919	West South Central	78,323
South Atlantic	11,123	Mountain	801
East North Central[b]	680,244	Pacific	1,261
West North Central[b]	225,819	Territories	1,633
	Total 1,039,624		

[a] Data from Scholl and Wallace (1952).

[b] Mehring (1948) reported that the total consumption in the North Central regions in 1940 was less than 55,000 tons.

Two types of raw phosphates are on the market at the present time:

Rock phosphate sold for direct application is the naturally occurring rock, which has been processed only to the extent of being finely ground. The principal constituent of most phosphate rock is fluorapatite. The fluorine content ranges from a trace to 3 to 4 per cent, with most samples showing more than 3 per cent. A good grade of rock phosphate will contain about 32 per cent total P_2O_5, with only a trace of the phosphorus water-soluble.

Colloidal phosphate is the trade name applied to low-grade rock phosphate or phosphatic clay which is a byproduct of the phosphate mining industry. In the hydraulic operation of mining rock phosphate, the clay containing some phosphate is washed into ponds and settles out. This material contains 18 to 23 per cent total P_2O_5. In all probability the phosphorus compounds in rock phosphate and colloidal phosphate are alike. Colloidal phosphate may be considered rock phosphate diluted with colloidal clay material. The material has been offered for sale under such names as Calphos, Vitaloid, Lonfosco, Min-Coll, Phosphate Colloids, Phos-Caloids, Waste Pond Phosphate, and perhaps others.

a. Factors Affecting the Availability of Raw Phosphates. The raw phosphates are water-insoluble and only slightly soluble in ammonium citrate (see Chapter X). Experience has shown that the response of

crops to the more insoluble phosphates has been inconsistent, whereas response to superphosphate on phosphorus-deficient soils has been consistent. A number of factors other than the phosphorus level of the soil may affect response to the raw phosphates.

(*1*) *Fluorine content.* Investigations by Hendricks *et al.* (1931) have shown that fluorine is a part of the raw mineral phosphate in all the deposits in the United States and in nearly all the important deposits outside the United States. It is now generally concluded that rock phosphate is primarily a mixture of fluorapatite and hydroxyapatite and that the compounds must be broken down in order to increase their usefulness as a fertilizer. Bartholomew (1935) studied the response of Sudan grass in the greenhouse to several raw phosphates of varying fluorine content. He found that natural phosphates containing the least fluorine produced the highest yields. It is interesting to note that the low fluorine phosphates came from Curaçao Island and that Hendricks *et al.* (1931) have shown that these deposits contain a compound that gives the same X-ray diffraction pattern as anhydrous tricalcium phosphate. According to Jacob *et al.* (1933), the fluorine content of most of the phosphate deposits of commercial importance is high.

(*2*) *Fineness.* As would be expected, the degree of fineness of raw phosphates affects their availability to plants to a certain extent. The same is true of some of the less-soluble processed phosphates. Most of the rock phosphate which is sold for direct application to the soil is ground so that 90 per cent or more will pass a 100-mesh sieve. Several investigators, including Burlison (1916), DeTurk (1926), Conner and Adams (1926), and Salter and Barnes (1935), have studied the effect of fineness of rock phosphate on its availability to plants. Their results show that in some cases finer particles than are found in the commercial product give a somewhat higher availability to plants. However, the increased availability does not seem to be great enough to justify grinding rock finer than the usual commercial product.

(*3*) *Soil reaction.* Research by Truog (1916), Conner and Adams (1926), Salter and Barnes (1935), Mooers (1929), Volk (1944), and Roberts *et al.* (1939) has shown that liming may decrease the availability of rock phosphate. Numerous experiments have shown that rock phosphate is of little or no value when applied to calcareous soils of the West. DeTurk (1942) states that free calcium carbonate may retard the intake of phosphorus from rock phosphate by plants which are not "strong feeders" on such form of phosphorus. He does not recommend, however, that lime be omitted where rock phosphate is used. Legumes that are "strong feeders" on rock phosphate need lime, and as a result the advantages of using limestone along with rock phosphate in a

legume rotation may exceed any early reduction in the yields of non-legumes. It is evident that only enough lime should be added to satisfy the needs of the legume to be grown.

(4) *Feeding power of plants.* The ability of various plants to utilize the phosphorus in rock phosphate is an important consideration in the interpretation of results. Merrill (1891), Truog (1916), Bauer (1921), Bartholomew (1928), DeTurk (1942), Odland and Cox (1942), and Brown and Jacob (1944) have shown that plant species differ in this respect. Results by Dickman and DeTurk (1940) show that corn plants made less growth and contained less phosphorus when grown in sand cultures containing 12 to 100 per cent rock phosphate than when grown in a sand culture which received a nutrient solution containing 20 p.p.m. of phosphorus. In general, it can be said that most of the cereals are poor feeders, whereas buckwheat and some legumes such as sweet clover, alfalfa, and red clover are strong feeders. It is fairly certain that satisfactory results from rock phosphate will not be obtained unless crops that are strong feeders are used in the rotation. These legumes may be counted on to increase the value of rock phosphate for other crops in the rotation. Brown and Jacob (1944) concluded from greenhouse and field tests that raw phosphates can be used to better advantage for long-season and perennial crops than for short-season crops.

(5) *Organic matter.* It has often been suggested that decomposing organic matter exerts a solvent action on raw phosphates and as a result increases its availability. Truog (1912) studied the effect of fermenting cow manure and grass vegetation on the solubility of rock phosphate. He found only a slight solvent action, which was always within the limit of experimental error. Bauer (1921) studied the effects of fermenting crop residues such as sweet clover, alfalfa, and buckwheat on the availability of rock phosphate, but the results failed to prove any solvent action. He found that in some cases organic matter and rock phosphate in pot cultures produced increases in the growth of corn larger than the sum of the increases obtained when each was applied separately. He concluded that the organic matter either had a solvent action on rock phosphate or that the phosphorus supplied by the organic matter gave the seedlings a better start so that they could utilize the phosphorus in rock phosphate to better advantage. Bray (1937) believes that the beneficial effect of adding organic matter with rock phosphate comes from the extra phosphorus added in the organic matter rather than from a solvent action on the rock phosphate. It should be pointed out, however, that strong feeders such as sweet clover can be used as green manure crops for the purposes of mobilizing the phosphorus in rock phosphate for use by crops that are not strong feeders.

(6) *Rate of application and phosphorus level of the soil.* In determining the value of rock phosphate, or any other source of phosphorus, the phosphorus level of the soil to be used and the rates of application are important factors in interpreting the results. Of course, sources of phosphorus cannot be evaluated on soils that give little or no response to phosphorus applications. In many cases where rock phosphate and superphosphate have been compared, they have both been applied at rates higher than needed for most economical returns. This point was recognized by Thorne (1916) in his summary of the field data on rock phosphate in the United States. He concluded that superphosphate proved to be a more effective as well as more economical source of phosphorus than rock phosphate where freight rates are a relatively large part of the cost of the materials. He also stated: "Where a different outcome has resulted it is usually found that one or both of the phosphate carriers have been used in such large quantity as to furnish more available phosphorus than the crops were able to utilize, thus making a comparative measurement of the effect of the two carriers impossible." Since rock phosphate is usually cheaper per unit of P_2O_5 than superphosphate, it is often compared with superphosphate when applied at two to four times the rate of P_2O_5.

b. Relative Efficiency of Raw Phosphates in the Different Regions of the United States. Numerous experiments show that raw phosphates will increase yields of most crops when applied to phosphorus-deficient soils. The important question is their relative efficiency in comparison to a standard source such as superphosphate. The best source for the farmer to use, of course, is the one that will produce the biggest crop yield for a dollar invested. In some of the early tests with rock phosphate, superphosphate was not included.

(1) *Experiments in the Northeast.* Some of the early field studies with rock phosphate date back to an experiment started by Professor W. H. Jordan of the Pennsylvania Agriculture Experiment Station in 1883. In 1916 a more comprehensive experiment comparing rock with superphosphate was initiated at State College, Pennsylvania, on a Hagerstown silt loam. Some of the data from this experiment, as reported by Noll and Irvin (1942), are presented in Fig. 1, covering the period 1922–1941. The data in Fig. 1 are from plots which had received approximately one-half ton of lime per acre per 4-year rotation. When the phosphates were applied with sodium nitrate and muriate of potash, 48 pounds of P_2O_5 from superphosphate produced as much wheat as 144 pounds of P_2O_5 from rock phosphate. Where manure was applied along with the phosphates, 24 pounds of P_2O_5 from superphosphate gave slightly higher yields of wheat than the lowest rate of rock phosphate,

which was 96 pounds of P_2O_5. It is interesting to note that the crop response to either source was greater when it was applied with other commercial fertilizer than when applied with manure. The manure itself supplied much of the needed phosphorus.

Lyon (1933) conducted a field test in New York on Dunkirk silty clay loam in which superphosphate, applied at one-fourth the rate of P_2O_5, produced as much crop increase as rock phosphate.

In a Rhode Island experiment started in 1894, rock and superphosphate were applied on an equal cost basis for the first 5 years. Then for

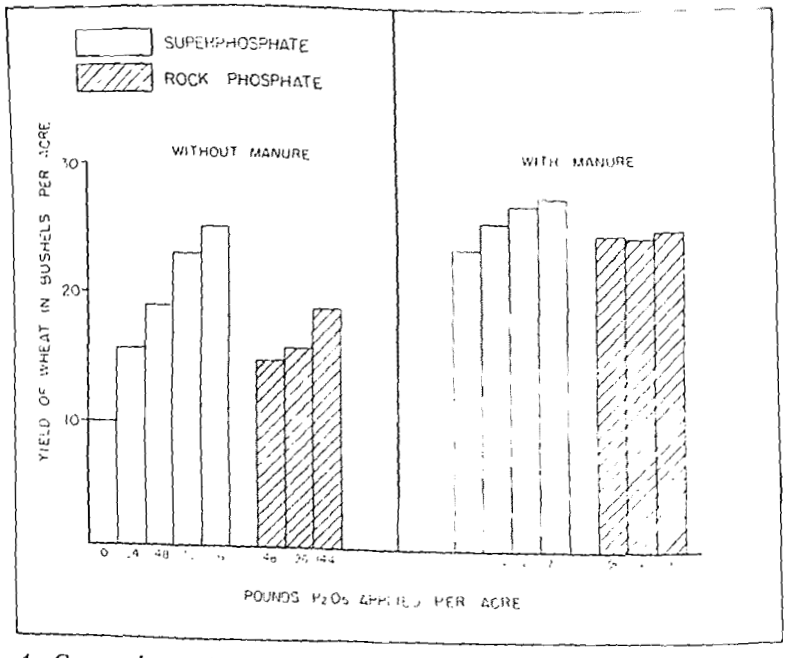


FIG. 1. Comparison of rock phosphate and superphosphate on wheat at various rates of application on Hagerstown silt loam in Pennsylvania.

the next 4 years the rate was modified so that at the end of this period all plots had received the same amount of P_2O_5. For the next 11 years it was carried as a residual study. In 1914 phosphates were again applied so that they could be compared on an equal P_2O_5 or an equal cost basis. On an equal cost basis the P_2O_5 from rock phosphate was 2.25 times the P_2O_5 from superphosphate. Starting in 1931 more finely ground rock phosphate was used and on an equal cost basis only 1.5 times as much P_2O_5 from rock phosphate as from superphosphate was used. The results from 1926 to 1939 were reported by Odland and Cox (1942). On limed plots, rock phosphate was less effective than superphosphate for the production of potatoes or corn when compared on either an equal P_2O_5 or an equal cost basis. Also, such crops as barley,

oats, parsnips, spinach, and endive grown for 1 year were more responsive to superphosphate. However, rock phosphate under all conditions produced higher yields of cabbage, carrots, and rape than did superphosphate.

In Maine, potatoes have been used as the test crop for evaluating the raw phosphates. Brown *et al.* (1944) conducted tests in 1931, 1932, 1937, and 1938 comparing colloidal phosphate and superphosphate for the production of potatoes grown on Caribou loam. The phosphates were applied at the rate of 160 pounds of P_2O_5 per acre. Superphosphate increased yields an average of 74 bushels, whereas colloidal phosphate gave yields only slightly better than no phosphorus. Brown and Hawkins (1944) compared colloidal phosphate, Tennessee brown-rock phosphate, and superphosphate for the production of potatoes at three locations. The average for the three locations shows that superphosphate increased yields 76 bushels, whereas colloidal phosphate increased yields 11 bushels and Tennessee brown-rock phosphate produced no increase.

(2) *Experiments in the Southeast.* The Kentucky Experiment Station has tested the value of superphosphate and rock phosphate on limed and unlimed land at five locations in the state. The tests were started between 1913 and 1919. Until 1930 rock phosphate was applied at a rate of 1600 pounds per 4-year rotation, whereas superphosphate was applied at 800 pounds. Each source was applied at these rates for two rounds of the rotation. After 1930 the rates were reduced one-half. The limed plots received 4 or 5 tons of lime during the first 8 years. A summary of the results from the Berea, Greenville, Mayfield, Farriston, and Campbellsville fields is given in Table II. The data show that on

TABLE II

RESPONSE OF VARIOUS CROPS TO SUPERPHOSPHATE AND ROCK PHOSPHATE IN TESTS CONDUCTED AT FIVE LOCATIONS IN KENTUCKY, 1913–1949[a]

Crop	Yield increases from superphosphate	Relative increases			
		Unlimed		Limed	
		Superphosphate	Rock phosphate	Superphosphate	Rock phosphate
Corn	14.6 bu.	100	138	148	140
Wheat	7.5 bu.	100	124	173	143
First-year hay	1309 lb.	100	156	209	209
Second-year hay	1208 lb.	100	159	178	218

[a] Data supplied by Weeks (1952, unpublished communication). Rock phosphate applied at four times the rate of P_2O_5 as superphosphate.

unlimed land rock phosphate was more effective than superphosphate when applied at four times the rate of P_2O_5. On limed land superphosphate was slightly better for corn and considerably better for wheat than rock phosphate. For first-year hay the two sources were about equal, but for second-year hay rock phosphate gave higher yields than superphosphate. In 1930 certain plots were divided in order to study residual effects of phosphates. The results presented in Table III con-

TABLE III

RESIDUAL VALUE OF SUPERPHOSPHATE AND ROCK PHOSPHATE IN TESTS CONDUCTED AT THREE LOCATIONS IN KENTUCKY[a]

Crop	Yield increases from superphosphate	Relative increases			
		Superphosphate		Rock phosphate	
		Continuous	Residual	Continuous	Residual
Corn	21.6 bu.	100	85	111	107
Wheat	12.3 bu.	100	59	97	84
First-year hay	2391 lb.	100	73	112	108
Second-year hay	1611 lb.	100	82	118	113
	Last four crops				
Corn	24.7 bu.	100	78	117	102
Wheat	11.2 bu.	100	51	96	84
First-year hay	2373 lb.	100	66	111	100
Second-year hay	1488 lb.	100	67	124	110

[a] Data supplied by Weeks (1952, unpublished communication). Rock phosphate applied at four times the rate of P_2O_5 as superphosphate.

tain data from limed and unlimed plots at Berea and from limed plots at Greenville and Mayfield. The data show that the yields of all crops decreased when superphosphate was omitted. The small drop in yields when rock phosphate was omitted is a reflection of the larger amount of P_2O_5 added in past years by rock phosphate. The results for the last 4 years of the residual period show a relatively greater decrease in yields when superphosphate was omitted than when rock phosphate was omitted (Weeks and Miller, 1948).

In a lime and fertilizer experiment conducted from 1927 to 1944 (Kentucky Agricultural Experiment Station, 1950), superphosphate was compared with rock phosphate on limed and unlimed land on the Western Kentucky Substation. Superphosphate was applied at 60 pounds of P_2O_5 per acre and rock phosphate was applied at 120 pounds. On unlimed land, rock phosphate produced 6.4 bushels more corn, the same amount of wheat, and 723 pounds more hay than superphosphate. On limed land (1 ton at beginning and 1 ton every 3 years), super-

phosphate produced 7.7 bushels more corn, 4.1 bushels more wheat, and 252 pounds more hay than rock phosphate. All plots received manure equal to the weight of crops removed except wheat grain. On the basis of the data it would appear that lime and superphosphate was a more economical treatment than rock phosphate either with or without lime.

In another test conducted at the Western Kentucky Substation from 1940 to 1949, different rates of concentrated superphosphate and rock

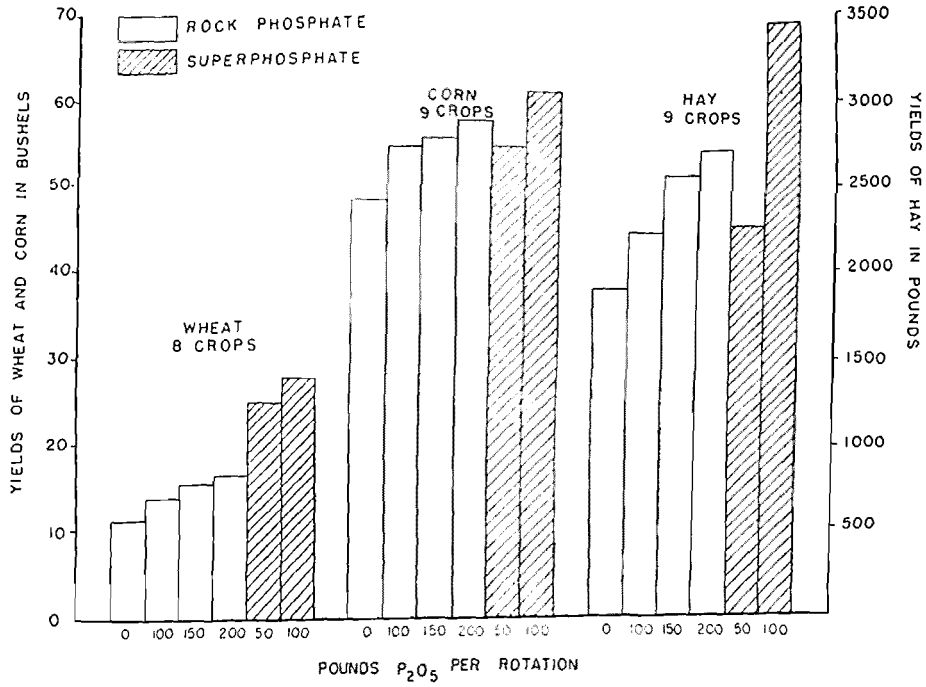


FIG. 2. Rock phosphate versus superphosphate in a 3-year rotation in Kentucky.

phosphate were compared. One ton of lime was applied at the beginning of a 3-year rotation of corn, wheat, and clover-grass hay and one-third ton per round of rotation thereafter. The results are presented in Fig. 2. The data show that 50 pounds of P_2O_5 from concentrated superphosphate produced about the same amount of corn and hay as 100 pounds of P_2O_5 from rock phosphate and almost twice as much wheat. Superphosphate applied at 100 pounds of P_2O_5 per acre produced more of all crops grown than 200 pounds of P_2O_5 from rock phosphate.

Mooers (1929) summarized the results of a 3-year rotation for a 10-year period of an experiment conducted at Crossville, Tennessee, in which superphosphate and rock phosphate were compared at several

rates. The soil was a friable loam of the DeKalb series and was deficient in lime and phosphate. Mooers calculated the most economical rate of each phosphate for the various crops. He then calculated the values of the yield increases after deducting the cost of phosphate when used at the most economical rate. These data are presented in Table IV. An

TABLE IV

THE CALCULATED VALUES OF THE CROP INCREASES AFTER DEDUCTION OF THE COST OF THE PHOSPHATE WHEN USED AT THE MOST PROFITABLE RATE IN TENNESSEE[a]

Crop	*Kind of phosphate*			
	Superphosphate		*Rock phosphate*	
	Unlimed	*Limed*	*Unlimed*	*Limed*
Corn	$ 8.70	$14.00	$11.50	$10.80
Potatoes	36.90	29.50	30.90	14.80
Oats	5.88	5.10	2.82	−2.04
Hay	5.80	10.40	3.20	1.40
Total	$57.28	$59.00	$48.42	$24.96

[a] Taken from Mooers (1929). In this study superphosphate was valued at about 6 cents per pound of P_2O_5 and rock phosphate at 1.5 cents per pound.

average of all crops shows that superphosphate was the more profitable source on limed or unlimed soil. Lime decreased the effectiveness of rock phosphate appreciably.

A number of experiments have been conducted by the Virginia Experiment Station in which superphosphate and rock phosphate were compared. The results of these experiments have been summarized by Rich and Lutz (1950) and are presented graphically in Fig. 3. Most of the experiments were conducted at one location for 5 years or more, and in some cases results are from long-time rotation experiments in which corn, small grain, and hay were used as test crops. The two sources were compared on an equal P_2O_5 basis. The data show that most crops did not respond as well to rock phosphate as they did to superphosphate. The yields of all crops were relatively high without the use of any phosphorus, and rock phosphate did not increase the yield of any crop very much. This fact is emphasized when "relative increases" for the various crops are calculated on the basis of increases from superphosphate as 100 per cent. ("Relative increase" as used in this paper is based on increase from superphosphate over no phosphate as 100. It should be noted that the term "relative yield" is also used but refers to the total yield from "x" phosphate as compared with the total yield from superphosphate as 100.) In the Virginia experiments the *relative increases* of

pasture herbage, wheat, red clover–timothy hay, alfalfa, corn, and cotton due to rock phosphate were 13, 43, 45, 69, 61, and 100 per cent, respectively.

Bartholomew (1950) of Arkansas reported the results of a 4-year rotation experiment in which superphosphate was compared with rock phosphate, the latter being applied at twice the rate of P_2O_5. The rotation included corn, oats, wheat, and red clover. Manure was added at

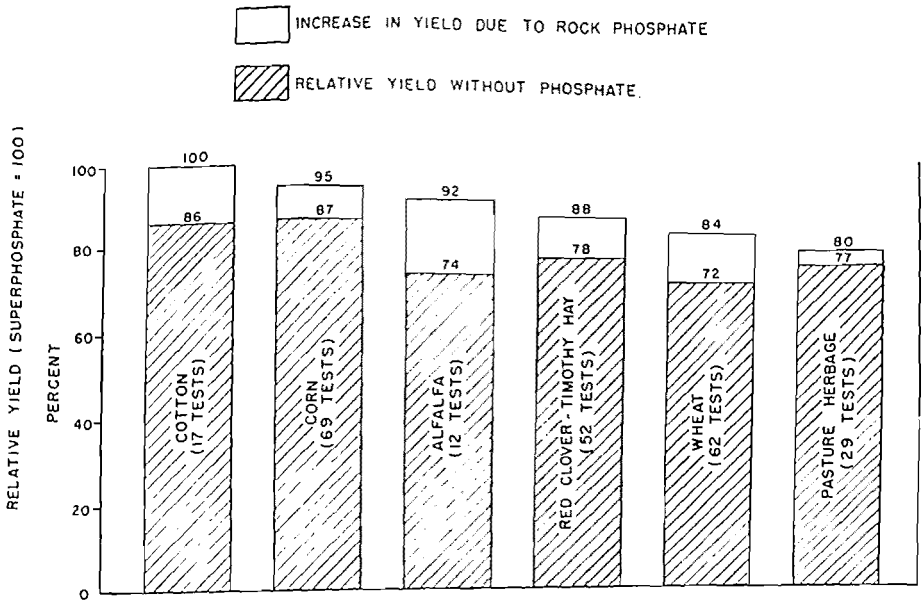


FIG. 3. Relative value of rock phosphate and superphosphate applied at equivalent rates of P_2O_5 on various crops in Virginia (Rich and Lutz, 1950).

rates equivalent to the weight of crops removed. On unlimed land during the first years of the experiment superphosphate produced higher yields than rock phosphate. After about 10 years the yields from the two sources were about equal for all crops except wheat. On limed land the yields of oats and wheat were higher from superphosphate throughout the period of the experiment. Corn yields were about the same from the two sources after the first 16 years; however, hay yields from rock phosphate never equalled the yields from superphosphate until the last rotation period. Except for corn during the last half of the period and red clover during the last rotation period, lime and superphosphate was more effective than rock phosphate with or without lime.

In 1930 a sources of phosphorus experiment in a rotation of corn and cotton with winter legumes was started at three locations in Ala-

bama (Ensminger, 1950). The results are presented in Table V. According to the data, 24 pounds of P_2O_5 from superphosphate was more effective in increasing the yields of cotton and winter legumes than 48 pounds of P_2O_5 from rock or colloidal phosphate or 96 pounds of P_2O_5 from rock phosphate. Colloidal phosphate was tested at the rate of 48 pounds of P_2O_5 only and appeared slightly more effective than 48 pounds of P_2O_5 from rock phosphate. Phosphate applications were discontinued after 1945 to study residual effects of the various sources. The data for the first 4 years of the residual period presented in Table V show that superphosphate produced as much cotton during the residual period as rock phosphate even though rock phosphate had been applied at higher rates of P_2O_5 from 1930 to 1945.

TABLE V

INCREASED YIELDS OF SEED COTTON AND WINTER LEGUMES FROM VARIOUS PHOSPHATES IN TESTS CONDUCTED AT THREE LOCATIONS IN ALABAMA

Source of phosphorus	P_2O_5 per acre to cotton and to winter legumes, pounds, 1930–1945	Average yield increases per acre: Green weight of winter legumes, pounds, 1930–1945	Seed cotton, pounds: 1930–1945	Seed cotton, pounds: 1942–1945	Seed cotton, pounds: Residual 1946–1949
Superphosphate	24	3539	202	288	166
Superphosphate	48	5471	256	324	184
Colloidal phosphate	48	2589	138	207	192
Rock phosphate	48	2275	89	131	102
Rock phosphate	96	3344	169	227	187
Superphosphate[a]	24	5142	268	340	177

[a] In addition to superphosphate, rock phosphate applied at rate of 2000 pounds per acre in 1930, 1936, and 1942.

In other tests yields of cotton at five locations in Alabama from 1923 to 1930 show that 96 pounds of P_2O_5 from superphosphate produced more cotton than eight times as much P_2O_5 from rock phosphate. This was true on both limed and unlimed land.

The Cullars Rotation on Norfolk loamy sand, which was started at Auburn, Alabama, in 1911, may be the oldest comparison of rock phosphate and superphosphate under way at the present time in the United States. One objective of the experiment was to study the value of superphosphate and rock phosphate for the production of crops in a rotation. Phosphate applications were discontinued after 1931 to study residual effects of the two sources. Cotton yields from 1911 to 1952 along with certain soil analyses are given in Table VI. It should be

TABLE VI

RESPONSE OF COTTON TO SUPERPHOSPHATE AND ROCK PHOSPHATE AND PHOSPHORUS CONTENT OF THE SOIL IN THE CULLARS ROTATION EXPERIMENT, AUBURN, ALABAMA

Source of phosphorus	Total P_2O_5 per acre applied, pounds, 1911–1931	Average yields of seed cotton per acre, pounds			P_2O_5 content of soil, p.p.m.		
		1911–1931	1932–1941	1942–1951	Dilute acid-soluble P_2O_5[a]	NH_4F-soluble P_2O_5[b]	Total P_2O_5
None	0	772	486	634	9	23	249
Superphosphate	914	1243	1111	1060	18	40	322
Rock phosphate	3654	1161	1197	1360	265	71	721

[a] Modified Truog method.
[b] Soluble in neutral 0.5 *N* ammonium fluoride solution.

noted that from 1910 to 1931 the rock phosphate-treated plots received four times as much P_2O_5 as the superphosphate-treated plots. Superphosphate produced slightly more cotton during the period when phosphate was being applied than did rock phosphate. During the first 10 years of the residual period, rock phosphate produced slightly more cotton than did superphosphate. During the last 10 years of the residual period, the yield was 300 pounds in favor of rock phosphate. It is evident from the phosphorus content of the soil samples taken in 1947 that the higher rate of rock phosphate caused a greater accumulation of total phosphorus as well as dilute acid- and ammonium fluoride-soluble phosphorus than did the lower rate of superphosphate. The soil data help to explain why lower yields were obtained from superphosphate than from rock phosphate in the last half of the residual period. In the experiment the higher application of P_2O_5 in the form of rock phosphate produced more oats and vetch than did superphosphate.

Clipping yields from eight pasture experiments in Alabama on acid soils show that colloidal phosphate produced less than half as much herbage as superphosphate when the two phosphates were applied on an equivalent cost basis. In three experiments on acid soils, colloidal phosphate applied at double the cost of superphosphate produced only about one-half as much herbage.

Woodhouse (1949) summarized the data from North Carolina showing the value of rock phosphate in comparison to superphosphate. He concluded that rock phosphate was inferior to superphosphate when applied on an equivalent P_2O_5 basis. Two to seven times as much phosphorus was required in the form of rock phosphate to give a response

equal to that of superphosphate. Red clover appeared to be more responsive to rock phosphate than corn or wheat.

In three pasture experiments in Mississippi, Anthony (1952) reported that rock phosphate applied at twice the rate of P_2O_5 as superphosphate increased yields 47 per cent as compared to 68 per cent for superphosphate. In another pasture experiment 200 pounds of superphosphate increased yields 140 per cent of the no-phosphate treatment, whereas 400 pounds of colloidal phosphate increased yields only 84 per cent. Average seed cotton yields at seven locations for 5 years showed that superphosphate increased yields 21 per cent while an equivalent amount of P_2O_5 from colloidal phosphate increased yields 5 per cent.

According to Bledsoe (1929), four raw phosphates, applied at the rate of 400 pounds per acre, produced 80 pounds less seed cotton than did one-half as much P_2O_5 in the form of superphosphate. In these tests in Georgia, which were conducted during the period 1921–1925, Florida pebble phosphate gave slightly higher yields than did either Tennessee blue rock or Florida soft rock phosphate. The Florida pebble phosphate, however, was finer than the other phosphates and contained more phosphorus than did Tennessee blue rock phosphate or Florida soft rock phosphate.

Results from Florida show that in some cases high rates of raw phosphates caused appreciable increases in the growth of pastures. Results reported by Blaser *et al.* (1941) indicate that Trifolium clovers (white, Persian, hop, red, and alsike) were more responsive to rock phosphate than were Medicago-Melilotus clovers (California bur, black medic, and Hubam sweet clover). Working with acid-peat soils, Neller (1945) found that 576 pounds of P_2O_5 from rock phosphate produced somewhat more herbage of carpet grass and Dallis grass than did 144 pounds of P_2O_5 from superphosphate. From tests conducted in central and western Florida, Neller *et al.* (1951) concluded that 2000 pounds of rock phosphate furnished adequate phosphorus for clover and grass on the Immokaloe and Rutlege fine sands of central and north Florida but not on the Tifton and Carnegie fine sandy loams of west Florida. It should be pointed out, however, that in these same tests one-sixth as much P_2O_5 in the form of superphosphate was also adequate.

(3) *Experiments in the Midwest.* The Indiana Agricultural Experiment Station conducted a number of field tests beginning in 1904 in which superphosphate and finely ground rock phosphate were compared. A summary of the results reported by Wiancko and Conner (1916) is presented in Table VII. They drew the following conclusions: "As a result of the eighty-two tests, it may be said most emphatically that it pays to use acid phosphate on the average Indiana soil under

average conditions. Raw phosphate has also shown a profit, but the profit is much smaller."

In 1897 the Ohio Experiment Station started a manure experiment including the use of superphosphate and rock phosphate. Although the pH of the soil at the beginning was not known, it was believed to be at least as low as 5.0. Liming was begun in 1905 and repeated in each rotation at the rate of 2 tons per acre. It was cropped to a rotation of corn, wheat, and clover. Salter and Barnes (1935) reported that even though rock phosphate was applied at twice the rate of P_2O_5 as superphosphate it was consistently less effective. Both materials were applied at a rate of 320 pounds per acre.

TABLE VII

SUMMARY OF INDIANA EXPERIMENTS IN WHICH SUPERPHOSPHATE AND RAW PHOSPHATE ARE COMPARED[a]

Crop and number of location-year tests	*Kind of phosphate*	*Pounds material applied per acre per year*	*Average yield per acre*	*Yield increase*
Corn (36 tests)	Superphosphate	190	43.04 bu.	5.49 bu.
	Raw rock	532	42.20 bu.	4.65 bu.
	None		37.55 bu.	
Wheat (33 tests)	Superphosphate	190	15.28 bu.	4.31 bu.
	Raw rock	532	12.88 bu.	1.91 bu.
	None		10.97 bu.	
Legume hay (9 tests)	Superphosphate	190	2998 lb.	320 lb.
	Raw rock	532	2773 lb.	95 lb.
	None		2678 lb.	
Potatoes (4 tests)	Superphosphate	500	112.0 bu.	29.4 bu.
	Raw rock	1000	94.2 bu.	11.6 bu.
	None		82.6 bu.	

[a] Data from Wianeko and Conner (1916).

The Ohio Station began a lime and rock phosphate experiment in 1905. A rotation of corn, oats, and hay was used. The hay crop was mainly red and alsike clovers through 1921. From 1922 to 1929 a mixture of sweet clover and alfalfa was used. In 1930 to 1933 alfalfa was grown on one half and sweet clover on the other half of each plot. The reaction of the soil at the beginning was about pH 5.3. Superphosphate and rock phosphate at a rate of 320 pounds of material per acre were compared on limed and unlimed land. Salter and Barnes (1935) re-

ported that on the unlimed land superphosphate produced somewhat higher yields of all crops as an average for the whole period, but slightly less hay from 1915 on than did rock phosphate applied at twice the rate of P_2O_5. Liming reduced the efficiency of rock phosphate somewhat as compared with superphosphate.

Salter and Barnes (1935) also reported the results of a 4-year rotation fertility experiment in which corn, oats, wheat, and clover were grown. Rock phosphate was applied to corn at three times the rate of P_2O_5 as superphosphate. For the period of 1915 to 1933 it was considerably less effective than superphosphate. The authors state that the reaction of the soil was rather acid at the beginning, but that repeated liming (2 tons per acre per rotation) had raised the pH to 7.2. The reaction of the soil was probably too high during the last part of the period to expect very much response from rock phosphate.

Hopkins of the Illinois Station first recommended the use of rock phosphate in 1903, basing his recommendation on results obtained by the Ohio and Maryland Stations. The Illinois Station soon started field tests to study the value of rock phosphate. However, most of the early tests did not include a comparison with superphosphate and will not be discussed here. Hopkins (1916) reported the results of three experiments conducted in southern Illinois in which 333 pounds of superphosphate was compared with 666 pounds of rock phosphate. Results from the period 1904 to 1915 show that on the Odin and Mascoutah fields rock phosphate at four times the rate of P_2O_5 gave somewhat higher yields than did superphosphate. On the Cutler field superphosphate was somewhat better than rock phosphate. The author pointed out that the increase in yields from phosphorus was scarcely sufficient to pay for the phosphates applied. Bauer *et al.* (1945) reported a summary of long-time field experiments conducted in Illinois from the beginning through the crop season of 1942. In 1924 five field experiments were modified for the purpose of comparing rock phosphate and superphosphate. The plots were divided and the original treatments continued on half of each plot. Superphosphate treatments were superimposed on the other half of unphosphated plots. The superphosphate was broadcast at an average annual rate of 160 pounds per acre, with most of it being applied before seeding wheat and some at corn planting. Superphosphate was compared with rock phosphate which was residual from 1924 on but had received 4 tons per acre from 1910 to 1924. On limed plots, superphosphate produced higher yields on the average than rock phosphate in both the manure and residues system. On unlimed plots in the residues system, rock phosphate was somewhat more effective than superphosphate. In a consideration of these results several points should be kept

in mind. First, most of the fields were not very responsive to phosphorus, and as a result neither source of phosphorus would show a profit in some cases. Second, rather small applications of superphosphate are being compared with a large residual amount of rock phosphate. Also, the superphosphate was applied broadcast, which may not be the most effective way to use this phosphate.

Bauer *et al.* (1945) reported data from other locations in which superphosphate and rock phosphate were compared. On the Carlinville field, 143 pounds of superphosphate was compared with 286 pounds of rock phosphate in a corn and wheat (sweet clover) rotation. On land that received 3000 pounds of lime per acre, superphosphate produced 18.9 bushels of wheat while rock phosphate produced 18.4 bushels of wheat. The unphosphated plots produced 10.6 bushels of wheat. These are average yields for the period 1922–1942. Superphosphate and rock phosphate were compared on limed land on the Ewing field. The following results were obtained as an average from 1922 to 1942:

Phosphate treatment annually	*Corn, bushels*	*Oats, bushels*	*Wheat, bushels*
None	26.6	20.7	9.6
62 lb. superphosphate	29.4	25.6	15.9
143 lb. rock phosphate	33.6	28.3	17.9

Crop residues were returned to the land. Lime was applied at an average annual rate of 571 pounds, and all plots received 100 pounds of muriate of potash annually. A corn, oats (Hubam-lespedeza), and wheat (sweet clover) rotation was used. The results were in favor of rock phosphate used at about four times the rate of P_2O_5 as superphosphate.

In tests conducted at the Joliet and Kewanee fields by Bauer *et al.* (1945), the two phosphates were compared on the basis of equal money values. At both locations totals of approximately 2700 pounds of rock phosphate and 1500 pounds of superphosphate were applied from 1928 to 1942. Wheat and clover-alfalfa were the test crops. The results include one crop of buckwheat because of a wheat failure. On the basis of crop values rock phosphate was somewhat better at Kewanee, but superphosphate was slightly better at Joliet.

Superphosphate and rock phosphate were compared in another test at the Kewanee field. The results as reported by Bauer *et al.* (1945) cover the period 1937–1942, in which four wheat crops and one clover-alfalfa hay crop were grown. The experiment was conducted on small field plots in randomized blocks replicated five times. Superphosphate applied at 300 pounds per acre in 1936, 1937, and 1939 produced

greater yields on both limed and unlimed land than did 300 pounds of rock phosphate.

(4) *Experiments in the West.* Field experiments have been conducted with raw phosphates on calcareous soils in most of the Western States. The following reports are typical. According to Toevs and Baker (1939) and Larson and Baker (1939) of the Idaho Station, rock phosphate was unsatisfactory as a source of phosphorus for alfalfa and a number of other crops. Little or no response was obtained from rock phosphate in experiments conducted in Montana by Green (1938) and Willis and Harrington (1939); Pittman and Thorne (1941) found that rock phosphate failed to increase crop yields in Utah; and according to Volkerding and Stoa (1947), rock phosphate was not a satisfactory source of phosphorus for North Dakota.

c. General Discussion. Raw phosphates are rather insoluble materials. Jacob *et al.* (1933) determined the solubilty of a number of raw phosphates ground to pass a 100-mesh sieve. Their results show that commercial types of raw phosphates in the United States contain from 0.3 to 2.5 per cent citrate-soluble P_2O_5 on the sample basis. Citric acid-soluble P_2O_5 ranged from 4 to 8 per cent. If the citrate solubility of phosphates has any significance in fertilizer control work, then the low solubility of raw phosphates would indicate a rather low availability to most plants. (See Chapter X.)

Numerous greenhouse experiments by Fudge and Fraps (1945), Volk (1942), Salter and Barnes (1935), McGeorge (1939), Lyon (1933), DeTurk (1942), and Jacob *et al.* (1935) have shown that raw phosphates are not satisfactory sources of phosphorus in pot cultures. It should be emphasized, however, that results from pot tests may not always be applicable to field conditions. In the first place, the limited space for root development probably puts greater stress on the applied phosphate than would be the case in the field. In the second place, plants are usually not grown to maturity in the greenhouse, which means that they are tested during the early stages of growth when they are relatively more responsive to readily available types of phosphorus. Also, in the greenhouse, rotations usually have not been used whereby legumes that are strong feeders on rock phosphate can be used to mobilize the phosphorus from raw phosphates.

In many of the field experiments the two carriers have been compared at only one rate; this makes it difficult to evaluate the results. In order to evaluate properly the two carriers of phosphorus, they should be tested at different rates so that the most economical rate of each can be determined.

Some workers have suggested that the addition of organic matter

such as manure increases the effectiveness of raw phosphates. From the data cited it is not possible to determine if this is true. It is evident, however, that in many cases manure furnished most of the phosphorus needed by crops, and as a result neither superphosphate nor rock phosphate gave appreciable yield increases over manure alone. Also, it is often claimed that rock phosphate is more effective when used on dark-colored surface soils than when used on light-colored soils. The dark-colored soils are probably better supplied with available phosphorus than the light-colored soils. On soils that are not very deficient in phosphorus, in many cases the rates of phosphorus used have been too high to show any differences between sources.

The effectiveness of raw phosphates is determined to a considerable extent by soil reaction. Lime frequently decreases the availability of rock phosphate. However, many of the legumes that are strong feeders on raw phosphates also respond to lime. Perhaps limestone and rock phosphate should not be applied at the same time in the rotation, or, if they are applied at the same time, they should be applied just ahead of alfalfa or sweet clover. It is certain that only as much lime should be used along with rock phosphate as is needed by the legumes to be grown.

DeTurk (1942) of the Illinois Station and others have suggested that superphosphate and rock phosphate be used as a team. He states that for some soils rock phosphate is the most economical source of phosphorus, but for other soils, and especially with certain crops, superphosphate may be necessary for optimum yields. The cost ratio of the two materials will determine the most profitable source to use. When some of the early field experiments were started, 1 pound of P_2O_5 from superphosphate cost about the same as 4 pounds of P_2O_5 from rock phosphate. In more recent years, the cost ratio at many points in Eastern United States has been about 1 pound of P_2O_5 in superphosphate to 2.5 pounds in rock phosphate.

3. *Mono-, Di-, and Tricalcium Phosphate*

The phosphates to be discussed in this section are the relatively pure calcium salts of orthophosphoric acid. Monocalcium phosphate ($Ca(H_2PO_4)_2 \cdot H_2O$) makes up about 80 per cent of the phosphorus in superphosphate. Dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$) is often referred to as reverted or precipitated phosphate and is an important constituent of ammoniated superphosphate. It may be produced by treating phosphoric acid with the proper amount of lime. Tricalcium phosphate ($Ca_3(PO_4)_2$) is the most insoluble of the calcium salts of phosphoric acid. Tricalcium phosphate may be formed by ammoniation of monocalcium phosphate. These phosphates are not used to any ap-

preciable extent in the relatively pure state as fertilizer materials. They do appear as important constituents of several materials which are widely used as fertilizers. It is evident, therefore, that information concerning these phosphates is basic to any studies of phosphate fertilizers.

A number of field tests have been conducted by the Alabama, Kentucky, and Virginia Stations in which these phosphates have been compared. A summary of these results is reported in Table VIII. Based on

TABLE VIII

RELATIVE EFFICIENCY OF CONCENTRATED SUPERPHOSPHATE, DICALCIUM PHOSPHATE, AND TRICALCIUM PHOSPHATE AS MEASURED BY CROP YIELDS IN ALABAMA, KENTUCKY, AND VIRGINIA[a]

State	*Crop*	*Number of location-year tests*	*Pounds of P_2O_5 per acre applied*	*Average yield per acre with concentrated superphosphate*	*Relative yields*		
					No phosphorus	*Dicalcium phosphate*	*Tricalcium phosphate*
Alabama	Cotton	358	60	956 lb.	76	102	97
Kentucky	Corn	86	15	38 bu.	71	95	91
Kentucky	Wheat	74	40	21 bu.	38	100	83
Kentucky	H y	61	0	3877 lb.	69	98	97
Virginia	Corn	48	36	55 bu.	84	99	95
Virginia	Wheat	29	36	21 bu.	72	94	89
Virginia	Red clover–timothy	15	25	2740 lb.	72	96	90
Virginia	Alfalfa	12	71	5208 lb.	74	96	95
Virginia	Pasture	29	48	4806 lb.	79	100	90
Total		712		Weighted averages		100	94

[a] Adapted from Ensminger (1950), Weeks (1952, unpublished communication), and Rich and Lutz (1950).

actual yields from concentrated superphosphate as 100 per cent, the data show that dicalcium was 94 to 106 per cent as effective, whereas tricalcium was 83 to 97 per cent as effective on the various crops. Wheat showed the lowest response to tricalcium phosphate of any of the crops tested. In Virginia and Kentucky the experiments were conducted on limed land.

Houghland *et al.* (1942) reported the results of field tests conducted in Maine, New Jersey, and Pennsylvania using potatoes as a test crop. Dicalcium phosphate was found to be practically as effective as concentrated superphosphate. Tricalcium phosphate was not included in these tests. The reaction of the soils ranged from pH 5.2 to 5.6.

Stanford and Nelson (1949) studied the response of oats to sources of phosphorus at three locations. Only on the Webster silty clay loam at

pH 6.0 was there a significant response to phosphorus. At this location dicalcium phosphate produced as much oats as did superphosphate. By the use of tagged superphosphate, they found that the percentage of plant phosphorus derived from dicalcium phosphate was much lower than that derived from superphosphate. (See Section III.)

At two locations in North Carolina, Hall *et al.* (1949) found no difference in yields of seed cotton produced by dicalcium phosphate and superphosphate. Radiophosphorus data, however, showed a much lower uptake of phosphorus from dicalcium phosphate than from superphosphate.

Odland and Cox (1942) reported the results of field tests in Rhode Island extending over a period of 6 years. They concluded that dicalcium phosphate gave about the same plant growth as superphosphate. An average of five hay crops showed that dicalcium phosphate produced slightly more hay than superphosphate on limed or unlimed soil. The same was true for potatoes grown 1 year.

According to results reported by Bauer *et al.* (1945), monocalcium, dicalcium, and tricalcium phosphates were about equally effective for the production of wheat. They were applied at an annual rate of about 23 pounds of P_2O_5 per acre.

Jacob and Ross (1940) reported the results of pot experiments conducted cooperatively by the Bureau of Plant Industry and five state experiment stations. Results of these experiments show that dicalcium phosphate was slightly more effective than superphosphate, whereas monocalcium phosphate was usually less effective than superphosphate.

Green (1938) reported the results of field tests with alfalfa, oats, and wheat conducted in Montana. Monocalcium phosphate produced lower yields than did concentrated superphosphate. Dicalcium phosphate was inferior to either concentrated superphosphate or monocalcium phosphate.

Olsen *et al.* (1950) reported results from field tests conducted on irrigated soils of the West in which several sources of phosphorus were compared. At one location where superphosphate and calcium metaphosphate increased the yield of sugar beets significantly, dicalcium phosphate produced a small increase but it was not statistically significant. Radiophosphorus data showed that dicalcium phosphate supplied less phosphorus to all crops grown than did superphosphate.

On the basis of crop yields, it appears evident that dicalcium phosphate is as good a source of phosphorus as is superphosphate on neutral and acid soils. A limited number of tests indicate that it is not a satisfactory source of phosphorus for calcareous soils. In general, tricalcium phosphate is less effective than monocalcium or dicalcium phosphates.

Under certain conditions liming would be expected to decrease the effectiveness of tricalcium phosphate.

4. Defluorinated Rock Phosphate

Jacob (1951) defines the term "defluorinated phosphate rock" as referring to "the products obtained by heating natural phosphates, usually phosphate rock, at high temperatures in the presence of silica and water vapor for the purpose of volatilizing the fluorine and converting the P_2O_5 into plant-available forms, chiefly alpha tricalcium phosphate." The class term has been used to cover products referred to as alpha phosphate, calcined phosphate, fused phosphate, fused phosphate rock, and fused tricalcium phosphate.

a. Fused Tricalcium Phosphate. Fused tricalcium phosphate is the preferred designation for a material which has been produced by the Tennessee Valley Authority since 1945 in a commercial-size furnace as a demonstration unit. This product, which contains 27 to 30 per cent P_2O_5, was described by Jones and Rogers (1949) and Walthall and Houston (1952). Fused tricalcium phosphate has been tested rather extensively on a variety of crops and soils in the United States (Alway and Nesom, 1944; Bauer *et al.*, 1945; Ensminger, 1950; Green, 1938; Houghland *et al.*, 1942; Jacob, 1944; Karraker, 1941; Long and Winters, 1951; Miller, 1952; Rich and Lutz, 1950; Terman, 1944; Toevs and Baker, 1939; Woodhouse, 1945).

The early work (Terman, 1944; Tennessee Valley Authority, 1946) showed that crop response to fused tricalcium phosphate was increased by lowering the fluorine content to about 0.4 per cent. The effect of particle size on crop response was subjected to intensive study in field tests. A comparison of 10-mesh (U. S. series) with 40-mesh material using pasture and other forage plants as indicator crops at eleven locations in seven Southeastern States (23 location-year tests) showed *relative increases* of 95 for the coarse product and 102 for the finer material.

A summary of the data from field tests conducted by the agricultural experiment stations of Alabama, Georgia, Kentucky, Mississippi, North Carolina, Tennessee, and Virginia is given in Table IX. As an average of 43 location-year tests, fused tricalcium phosphate on permanent pasture mixtures gave a *relative increase* of 106. The *relative yield* value of 60 for the no-phosphate treatment shows that these tests were conducted on phosphorus-deficient soils. Various mixtures of pasture species were used, all of which included white clover as the dominant legume. Long and Winters (1951) pointed out that in some of the individual tests 10-mesh fused tricalcium phosphate was slow in taking

effect on pasture sods on extremely deficient soils. The yields show, however, that this product, when ground to pass a 40-mesh sieve, compares favorably with superphosphate as a source of phosphorus for white clover-grass mixtures on the acid soils of Southeastern United States.

TABLE IX

RELATIVE EFFICIENCY OF FUSED TRICALCIUM PHOSPHATE (FTP) FOR VARIOUS CROPS ON ACID SOILS[a]

Mesh size of FTP	*Crop*	*Number of states*	*Number of locations*	*Number of location-year tests*	*Relative yield without P*[b]	*Relative increase with FTP*[c]
10 or 40	Permanent pasture mixture	6	18	43	60	106
40	Small grain	6	33	76	65	92
40	Corn	5	46	74	76	95
40	Cotton	2	13	24	65	86

[a] Soils of the Tennessee Valley States of Alabama, Georgia, Kentucky, Mississippi, North Carolina, Tennessee, and Virginia. Original data from the state agricultural experiment stations.

[b] Based on a value of 100 for actual yield with concentrated superphosphate.

[c] Based on an increase in yield of 100 for concentrated superphosphate over no phosphate.

On the other hand, the mean values in Table IX for small grain, corn, and cotton show that this phosphate is not so effective on these crops as superphosphate. Fused tricalcium phosphate gave average *relative increase* values of 92 on small grain, 95 on corn, and 86 on cotton. The 174 location-year tests were conducted on phosphorus-deficient soils, as shown by *relative yield* values of 65, 76, and 65 for the no-phosphorus treatment on small grain, corn, and cotton, respectively.

The importance of time of application in obtaining crop response to fused tricalcium phosphate was illustrated in a rotation experiment reported by Long and Winters (1951). Figure 4 shows a comparison of fused tricalcium phosphate with superphosphate on corn on a highly deficient soil in Tennessee. This phosphate was only 65 per cent as effective as superphosphate on corn yields the first year after starting the rotation of corn, oats, and red clover; after the first year, however, fused tricalcium phosphate increased yields as much as superphosphate, giving *relative yield* values on corn of 102, 90, and 100 for the last 3 years of the experiment.

In contrast to the generally favorable results on acid soils, tests on alkaline or calcareous soils show conclusively that fused tricalcium phosphate is not a satisfactory source of phosphorus for these conditions

(Green, 1938; Jacob, 1944; Larson and Baker, 1939; Toevs and Baker, 1939).

b. Calcined Phosphates. These phosphates have been described by Jacob (1944) as porous, easily ground materials obtained by heating phosphate rock at sintering temperatures. These phosphates are distinguished from the fused products which are made by melting the rock



FIG. 4. A comparison of concentrated superphosphate and 10-mesh fused tricalcium phosphate at the rate of 120 pounds P_2O_5 per acre on corn. *Left*, concentrated superphosphate; yield, 47 bushels. *Right*, fused tricalcium phosphate; yield, 31 bushels. Plateau Experiment Station, Crossville, Tennessee, photographed July 13, 1948. In 1949, 1950, and 1951, these phosphates were of equal effectiveness on corn yields in this same experiment. (Photograph courtesy of Tennessee Agricultural Experiment Station.)

at higher temperatures to give a dense, nonporous material on cooling.

In general, calcined phosphates have performed similarly to fused tricalcium phosphates when materials of similar fineness have been compared. Bauer *et al.* (1945), Houghland *et al.* (1942), and Ross and Jacob (1937) reported data to show that finely ground calcined phosphate was nearly as effective as superphosphate on acid to neutral soils. Studies by Ross and Jacob (1937) indicated that material coarser than 40-mesh was inferior to a more finely ground product.

Toevs and Baker (1939), Olsen *et al.* (1950), McGeorge (1939),

Larson and Baker (1939), and Jacob (1944) studied crop response to calcined phosphates on alkaline soils and concluded that this form was inferior to superphosphate for these conditions.

5. *Metaphosphates*

a. Calcium Metaphosphate. Jones and Rogers (1949) described the agronomic characteristics of calcium metaphosphate and showed the essential steps in the process of production in a simple flow diagram. A typical sample of calcium metaphosphate as produced by the Tennessee Valley Authority in a demonstration scale plant and tested over a period of years by the state agricultural experiment stations was analyzed as follows:

P_2O_5, *per cent*		
Total	*Citrate-soluble (80-mesh material)*	*CaO, per cent*
63	62	27

Screen analysis, cumulative per cent through		
10-mesh	*20-mesh*	*100-mesh*
100	80	20

Williams and Reith (1948) reported unfavorable results on turnips on Scottish soils with a material described as calcium metaphosphate. The material used in these tests, however, was quite different in solubility from the calcium metaphosphate used extensively in greenhouse and field tests in the United States. It was reported to be only 15 per cent soluble in citric acid, although more than two-thirds of the material was finer than 100-mesh.

Recent field experiments in Iowa (Pesek, 1952, personal communication) and Tennessee (Long, 1952, personal communication) suggest that there may be an advantage to grinding calcium metaphosphate finer than 10-mesh.

Experiments on several of the more extensive soils in the humid region of the United States showed calcium metaphosphate to be generally satisfactory as a source of phosphorus for field crops (Brown and Clark, 1943; Bauer *et al.*, 1945; Chandler and Musgrave, 1944; Ensminger, 1950; Houghland *et al.*, 1942; Midgley and Dunklee, 1945; Miller, 1952; Rich and Lutz, 1950; Ross and Jacob, 1937; Roberts *et al.*, 1942; and Woodhouse, 1945).

(1) Tests in the Tennessee Valley States. Mean *relative yield* values are shown in Table X for a large number of field experiments conducted in the Tennessee Valley States with corn, cotton, legume hay, and wheat. A 10-mesh product with fines left in was used in these

tests. Calcium metaphosphate was fully as effective as superphosphate on the acid soils used in these experiments, which involved the following number of location-year tests: 264 on cotton, 195 on corn, 175 on wheat, and 124 on legume hay. Included in the summary in Table X

TABLE X

CROP RESPONSE TO 10-MESH CALCIUM METAPHOSPHATE AS COMPARED WITH SUPERPHOSPHATES IN FIELD EXPERIMENTS IN THE TENNESSEE VALLEY STATES, 1934–1944[a]

Source of phosphorus	*Relative yields*[b]			
	Cotton	*Corn*	*Legume hay*	*Wheat*
Concentrated superphosphate	100	100	100	100
No phosphorus	82	82	74	59
16–20% superphosphate	102	102	99	99
Calcium metaphosphate[c]	99	100	100	99

[a] Values calculated from data reported by Tennessee Valley Authority (1946). Original data from the state agricultural experiment stations.

[b] Based on a value of 100 for actual yield with concentrated superphosphate.

[c] Averages of 264 tests on cotton, 195 on corn, 175 on wheat, and 124 on legume hay.

were the results of extensive rotation experiments in Virginia. O'Brien (1944) reported that in corn–wheat–hay rotations—with corn and wheat receiving 36 pounds of P_2O_5 per acre and the hay crop utilizing residual phosphate—calcium metaphosphate ranked as high or higher than superphosphate at six of the nine locations. Likewise, Woodhouse (1945) concluded that calcium metaphosphate was as satisfatcory as concentrated superphosphate in a 6-year experiment involving different rates of P_2O_5 on a white clover-grass sod in North Carolina.

(2) *Tests in the Midwestern States.* A 7-year experiment on Bedford silt loam in Indiana involving a rotation of corn, wheat, and hay provides some interesting data on calcium metaphosphate. The average yields of a no-phosphate treatment which included lime (soil pH 6.2), manure, potash, and nitrogen were 48 bushels of corn and 2,784 pounds of hay per acre. Average increases in crop yields from superphosphate and calcium metaphosphate, each applied at a rate of 48 pounds of P_2O_5 per acre per rotation, were reported by Enfield (1949, personal communication) as follows:

Source	*Corn, bushels/acre*	*Wheat, bushels/acre*	*Hay, pounds/acre*
Calcium metaphosphate	9.6	13.7	1,241
20% superphosphate	8.7	7.0	1,107

These results show increases in yields of these crops where calcium metaphosphate was used to be fully as great as increases resulting from the use of superphosphate.

Using alfalfa as a test crop in Minnesota, Alway and Nesom (1944) compared calcium metaphosphate with superphosphate on a field of Clarion clay loam, the surface soil of which was slightly acid. When applied on the plowed land in advance of seeding, calcium metaphosphate increased the yield virtually as much as did superphosphate for the next three crop seasons. When spring top-dressed on an established stand, however, metaphosphate was inferior to superphosphate the first season, but almost equally effective in the second year. The Minnesota Experiment Station workers have suggested that the effectiveness of calcium metaphosphate may be increased by working it into the soil well in advance of seeding.

The importance of recognizing soil differences in the use of calcium metaphosphate is well illustrated by a report from the Iowa Agricultural Experiment Station (1947). In an experiment on calcareous Ida silt loam, calcium metaphosphate was less effective in increasing corn yields than was superphosphate, but when applied to slightly acid Monona silt loam (pH 6.5), this phosphate was fully as effective as superphosphate. Likewise, calcium metaphosphate compared favorably with superphosphate on oats on Webster silty clay loam (pH 6.0) in other tests in the same state (Stanford and Nelson, 1949).

(3) *Tests in the Western States.* Experiments conducted in the Western States are not conclusive as to the effectiveness of calcium metaphosphate on alkaline or calcareous soils. This phosphate has been tested on alfalfa in Montana (Green, 1938), New Mexico (Hinkle, 1942a) and Idaho (Toevs and Baker, 1939), and on sugar beets, wheat, and barley in Colorado (Olsen *et al.*, 1950). In some of these tests, calcium metaphosphate gave responses equivalent to those of superphosphate, but in others it was decidedly inferior. More research will be needed to determine the factors which influence the response of crops to calcium metaphosphate on the calcareous soils. This phosphate is much more effective on alkaline soils than the forms of tricalcium phosphate which have been tested, but until more is known about the effects of placement, time of application, particle size, soil moisture, and possibly soil type, it is not as dependable as the water-soluble phosphates.

b. Potassium Metaphosphate. This phosphate contains about 55 per cent P_2O_5 and 35 per cent K_2O. Potassium metaphosphate is only slightly soluble in water but apparently hydrolyzes readily in the soil.

A recent summary of the data from 46 location-year tests on acid

soils in five states (Tisdale, 1952, personal communication) comparing potassium metaphosphate with concentrated superphosphate showed a mean *relative yield* value of 101 for potassium metaphosphate. In these same tests the no-phosphorus treatment had a mean value of 67.

Brown and Clark (1943), Chandler and Musgrave (1944), Ensminger (1950), Houghland *et al.* (1942), and The Idaho Agricultural Experiment Station (1943) reported somewhat superior responses to potassium metaphosphate over those obtained with superphosphate or with any other form of phosphorus used in the various tests. These reports suggest an advantage to the low water-solubility of the potassium or to having potassium and phosphorus present in each particle of the fertilizer. Possible beneficial effects of multiple-nutrient granules in fertilizers will be mentioned in a discussion of the nitric phosphates in Section II.8.b.

c. Other Metaphosphates. The Idaho Agricultural Experiment Station (1943) reported on greenhouse tests which included a potassium-calcium metaphosphate. As an average of four crops, this phosphate produced a *relative yield* of 100 when compared with concentrated superphosphate as the standard. McGeorge (1939) reported that sodium metaphosphate was "extremely effective" as a source of phosphorus for plant growth.

6. Byproduct Phosphates

a. Basic Slag. Basic slag contains varying amounts of P_2O_5, depending upon the phosphorus content of the iron ore used in the manufacture of steel, from which industry it is a byproduct. The current production in this country contains 8 to 10 per cent total P_2O_5, 60 to 90 per cent of which is soluble in ammonium citrate. Basic slag, referred to also as Thomas slag, has been used in Europe as a fertilizer for many years. It has been produced in significant quantities in the Birmingham, Alabama, district in the United States since about 1915. As a liming material, basic slag is generally rated as 50 to 65 per cent as effective as a good grade of ground limestone.

The availability of the phosphorus in basic slag has been investigated on the major crops and for a wide range of soil conditions both in Europe and in the United States. Ensminger (1950) summarized the data from 15-year experiments and numerous short-duration tests conducted in Alabama from 1920 to 1945. *Relative increase* values for basic slag in comparison with superphosphate in the long-term rotation experiments at four locations were 85, 114, and 94 on cotton, corn, and winter legumes, respectively. Similar 15-year experiments at five locations without a winter legume crop showed a *relative increase* value of 83 for basic slag on cotton. As an average of 222 short-duration tests,

basic slag produced 852 pounds of seed cotton as compared with 914 pounds from superphosphate. Thus, the Alabama data show basic slag to be inferior to superphosphate on cotton, having a *relative increase* value between 85 and 90 when used on this crop. It was more effective on corn, winter legumes, and pastures. Similar results were reported by Rich and Lutz (1950), who concluded from 26 to 30 tests in Virginia with each of four crops—corn, wheat, hay, and pastures—that the *relative yield* values for basic slag ranged between 91 and 95.

Studies by Andrews (1942), Salter and Barnes (1935), Paauw (1950), and Scharrer (1950) show fairly conclusively that basic slag is less effective than the water-soluble phosphates on heavily limed or alkaline soils. Salter and Barnes (1935) in Ohio reported that the *relative increase* values for basic slag dropped from 85 on cereals and 140 on clovers on unlimed land to 0 on corn, 70 on oats, and 85 on clover on soils limed to pH 7.5. Roberts *et al.* (1939) in Kentucky, Hartwell and Damon (1927) in Rhode Island, Mooers (1929) in Tennessee, and Neller (1945) in Florida reported data from field experiments with slag on a variety of agronomic and horticultural crops which showed this phosphate to be about as effective on acid soils as was superphosphate when liberal applications are made over a period of years.

b. Bone Meal. Crushed bone was one of the first materials to be used as a source of plant nutrient phosphorus. For a period of time the fertilizer industry used bone meal as a raw material in the manufacture of superphosphate. Although bone meal is used today in this country mostly as an animal feed supplement, 85,000 tons of bone meal were used as fertilizer as late as 1937.

Rich and Lutz (1950) showed the *relative yield* of bone meal as 83 on wheat and 89 on red clover-timothy hay as averages of 29 location-year tests in Virginia. Corn—a low phosphorus-responding crop—showed a value of 98 for bone meal as an average of 17 tests.

Salter and Barnes (1935) showed that bone meal, similar to other forms of tricalcium phosphate, was less effective on heavily limed soil. They showed a *relative increase* value of 80 for bone meal on cereal crops on unlimed land and a value of only 20 on soil at pH 7.5. Odland and Cox (1942) reported values for bone meal that compared favorably with superphosphate on potatoes but compared unfavorably on oats and barley. Bone meal was more effective than superphosphate in a 20-year experiment in Pennsylvania (Noll and Irvin, 1942) and in a 25-year wheat test on Sanborn Field in Missouri (Smith, 1942). Williams and Reith (1948) concluded from tests in Scotland that three different forms of bone meal were about as effective as superphosphate on turnips, swedes, and potatoes.

7. *Miscellaneous Phosphates*

a. Rhenania or Silicophosphate. According to Crowther and Lea (1946), the process of heating ground mineral phosphate with soda ash and sand in the presence of steam was first used commercially in Belgium in 1916. Since then Rhenania phosphate has become an important source of fertilizer phosphorus in Germany, competing successfully with superphosphate and basic slag. The product is made by sintering the mixture at about 1300 to 1400° C., this removes most of the fluorine from the mineral phosphate.

These products have also been referred to as silicophosphates and contain normally about 33 per cent total P_2O_5, which is not water-soluble but is nearly all citrate-soluble. The material is reported to be a mixture of calcium silicophosphate and calcium sodium phosphate. Crowther and Lea (1946) and Crowther and Cooke (1951) summarized the results of field experiments with several experimental grades of silicophosphate which were conducted in Great Britain. They concluded, from 130 field tests distributed over England, Wales, Scotland, and Northern Ireland, that for swedes and potatoes on very acid soils (pH less than 5.5) the silicophosphates were fully as effective as superphosphate. On less-acid and neutral soils, superphosphate was superior as a source of phosphorus. For example, the silicophosphates were only about two-thirds as effective as superphosphate on potatoes on soils with a pH greater than 5.5.

Scharrer (1950), reviewing tests with Rhenania phosphate in Germany, concluded that this material was a better source of phosphorus on acid soils than superphosphate and was more effective than basic slag on alkaline soils. Jacob and Ross (1940) studied the earlier reports on citrate-soluble phosphates prepared by heating rock phosphate with alkali salts and concluded that these materials were excellent sources of phosphorus.

b. Rock Phosphate-Magnesium Silicate Glasses. Mixtures of rock phosphate and serpentine or olivine have been fused to make glass-like products containing from 20 to 24 per cent P_2O_5. Two developments on the West Coast of the United States led to commercial production of fertilizers by this process for a short time, but operations have been discontinued.

Hill *et al.* (1948) tested seven different glasses of this type in pot cultures. These tests showed a marked effect of particle size of the material on availability. When finely ground, these glasses compared favorably with superphosphate on acid soils but were less effective on calcareous soils. These workers concluded that these glasses should be

ground to pass a 60-mesh sieve. Holmberg *et al.* (1944–1949) reported on field trials in California with a product made from rock phosphate and serpentine, and Tremblay and Baur (1952) gave results of experiments in western Washington with a rock phosphate-olivine glass. Using rapid-growing annual vegetable crops, these workers concluded that these phosphates were not so effective as the more-soluble phosphates.

c. Liquid Phosphoric Acid. Direct use of H_3PO_4—principally in irrigation water—has gained some importance in the Western States in recent years. Olsen *et al.* (1950) working with alfalfa and Thorne (1944) with potatoes reported satisfactory results with liquid phosphoric acid. On the other hand, Converse (1948) observed that this form of phosphorus appeared to leach out of coarse-textured soil on the Yuma Mesa in Arizona more than superphosphate. The phosphorus in this form has been generally as effective as, but not superior to, superphosphate on the soils in the Western States where it is being used.

d. Sodium and Potassium Phosphates. Ensminger and Cope (1947) reported 16-year average yields of cotton in Alabama which showed monosodium phosphate to be decidedly inferior to superphosphate on unlimed soil, but only slightly inferior on limed soil. Stewart (1952) concluded that for the acid soils of Great Britain disodium phosphate was about as effective as superphosphate on swedes, turnips, and pastures. Mehring (1953) stated that trisodium phosphate was an excellent source of plant nutrient phosphorus on acid soils, and Weiser (1933) gave 3 years of data which were favorable to sodium phosphate on pasture plants. Studies by Spencer and Stewart (1934) convinced these workers that disodium phosphate would penetrate soils better than superphosphate. Potassium dihydrogen phosphate has been used frequently as a source of readily available phosphorus in pot cultures.

e. Organic Phosphates. A wide variety of organic compounds containing phosphorus have been tested by the Neubauer technique and in solution and soil cultures in the greenhouse. Only a few have been subjected to field tests. Among those tested by Allison *et al.* (1941) and MacIntire *et al.* (1948) for availability were the glycerophosphates; hexose diphosphate; nucleic acid and its sodium salt; mono-, di-, and triphenyl phosphates; hexaethyl tetraphosphate; monoethyl, triethyl, and tricresyl phosphates. Triethyl phosphate was of no value as a fertilizer. Tricresyl and triphenyl phosphates induced some growth of grasses but were inferior to superphosphate. All the other organics listed were about as available as monocalcium phosphate.

In a field test in Illinois Bauer *et al.* (1945) reported wheat yields for a 4-year period which gave calcium and sodium glycerophosphates

relative increase values of 81 and 84, respectively. Pinck *et al.* (1941) and Spencer and Stewart (1934) studied penetration and rates of mineralization of organic phosphates in soil and concluded that certain forms, including calcium diethyl phosphate, appeared to resist soil fixation longer than inorganic forms. Rogers *et al.* (1940) showed that in culture solutions phytin and lecithin were available to plants, and that nucleic acid and calcium glycerophosphate were readily mineralized by exoenzyme systems on corn roots and by soil catalysts.

f. Other Phosphates. Some of the miscellaneous inorganic materials which have been tested as sources of plant nutrient phosphorus and appear to have fairly good availability include the following: spent phosphate catalysts (Armiger *et al.*, 1947); superphosphate made with sludge acid and alkylation acid from the petroleum industry (Brown *et al.*, 1943; Jacob and Armiger, 1944); and monocalcium chlorophosphate made by treating rock phosphate with a mixture of hydrochloric and phosphoric acids (Houghland *et al.*, 1942). McGeorge (1939) reported that pyrophosphate was readily available to plants. The Tennessee workers (MacIntire *et al.*, 1950), on the other hand, found phosphorous acid and the phosphites definitely toxic to plant growth.

Truog (1916) pointed out that aluminum phosphate was utilized to a considerable degree by plants in pot cultures; ferric phosphate was less consistent in increasing plant growth; and ferrous and manganous forms were generally poor sources of phosphorus.

8. Phosphorus-Nitrogen Fertilizers

a. Ammonium Phosphates. Monoammonium phosphate is produced commercially for use as a fertilizer either in the form of a single compound analyzing about 11 per cent N and 48 per cent P_2O_5 or in mixtures with ammonium sulfate containing about 16 per cent N and 20 per cent P_2O_5. There is little question about the availability of the phosphorus in either of these materials.

Likewise, diammonium phosphate, which has been produced only on a pilot-plant scale in this country, is readily available to crops. This phosphate, however, has been used in Europe for some time both as a straight material and as a component of some of the nitrophoskas. The ammonium phosphates have been tested rather extensively in Western Canada (Mitchell *et al.*, 1952) and in some of the Western States in this country (Griffiths and Finch, 1945; Hinkle, 1924b; Olsen *et al.*, 1950). From the results of 199 location-year tests in Alabama, Ensminger (1950) concluded that, when dolomite was added to neutralize the acidity and ammonium sulfate to supply needed sulfur, both mono- and diammonium phosphates were about as effective on cotton yields

as was superphosphate. A 16-year test, however (Ensminger and Cope, 1947), showed the importance of neutralizing the acidity of these forms of phosphorus. When lime was omitted, monoammonium phosphate produced less cotton than the no-phosphate check plots. Likewise, Salter and Barnes (1935) and Weiser (1933) showed that the relative efficiency of this phosphate increased markedly by liming the soil.

The ammonium phosphates appear unusually well adapted for use on alkaline or calcareous soils because of their high solubility, combination of nitrogen and phosphorus (both of which are frequently needed), and residual acidity.

b. Nitric Phosphates. The potential economy in processes involving the acidulation of rock phosphate with nitric acid is based on the dual role of nitric acid in dissolving rock phosphate and also in furnishing plant nutrient nitrogen.

Hignett (1951) and Walthall and Houston in Chapter XII described modifications of the basic process involving acidulation of rock phosphate with nitric acid alone or with mixtures of nitric and phosphoric or sulfuric acids. The Tennessee Valley Authority products were first called "nitraphosphates," but more recently the preferred designation has been "nitric phosphates."

Rogers (1951) compiled the data from ten state agricultural experiment stations on the efficiency of the NP and NPK products made by the nitric-phosphoric and nitric-sulfuric acidulation of rock phosphate. Table XI presents a summary of the results of field experiments on corn, wheat, oats, and cotton conducted during the period 1949–1951 in six states in the Southeastern United States. The following conclusions can be drawn:

1. The phosphorus in the nitric phosphates is as available as concentrated superphosphate to corn, cotton, and small grain on acid soils in the Southeastern United States. Also on these soils, the nitric phosphate products containing nitrogen, phosphate, and potash were fully as effective as commercial-type mixtures of similar NPK ratios for corn and cotton.

2. Water-solubility. There is no evidence that water-solubility greater than about 10 per cent is required in the nitric phosphates for small grain, corn, and cotton on the soils of the Southeast. Very limited tests in Iowa and Nebraska, however, suggest that the nitric phosphates of low water-solubility may be somewhat less effective on alkaline soils than the more-soluble superphosphate. Observations were made also which indicate that water-solubility may be more important on soils extremely deficient in native phosphorus and under adverse climatic conditions.

TABLE XI

COMPARISON OF CONCENTRATED SUPERPHOSPHATE (CSP) AND NITRIC PHOSPHATE (DNP) AS SOURCES OF PHOSPHORUS FOR CORN, SMALL GRAIN, AND COTTON ON ACID SOILS OF SOUTHEASTERN UNITED STATES, 1949–1951[a]

Crop	*Fertilizer comparison*[b]	*Number of locations*							*Base yield/acre (CSP)*[c]	*Relative yield*[d]		*Relative increase (DNP)*[e]
		Ala.	*Ga.*	*Ky.*	*Miss.*	*Tenn.*	*Va.*	*Total*		*No P*	*DNP*	
Corn	CSP vs. DNP (14–14–14)	3	3	4		11	1	22	61.0 bu.	63	99[f]	98
Corn	CSP vs. DNP (11–11–11)	3	1	2		8	1	15	56.7 bu.	68	97[f]	91
Wheat	CSP vs. DNP (14–14–14)		2	2		2	2	8	19.6 bu.	49	107[f]	113
Oats	CSP vs. DNP (14–14–14)				5	1		6	Miss., 1966 lb., Tenn. 35.5 bu.	61	104[f]	109
Cotton	CSP vs. DNP (11–11–11)	1			2	2		5	886 lb.	42	112	121
Cotton	CSP vs. DNP (14–14–14)	1			2	2		5	886 lb.	42	98	97

[a] Adapted from Rogers (1951). Original data from the state agricultural experiment stations.

[b] CSP (concentrated superphosphate) used as standard source of phosphorus; nitrogen from ammonium nitrate; and potassium from potassium chloride.

[c] Yields in pounds of seed cotton and bushels of grain, except Mississippi, which is in pounds of dry forage for oats.

[d] Based on a value of 100 for actual yield with CSP.

[e] Based on a value of 100 for increase in yield from CSP over no phosphate.

[f] Odds are approximately 10:1 that DNP 14–14–14 was more effective than CSP on small grain and considerably less than 10:1 that DNP was less effective than CSP on corn.

3. Particle size. The 12- to 50-mesh range in size of particles appears to be about optimum for these materials. There was definite indication that particles coarser than 12-mesh were less effective and some evidence that material finer than 40-mesh was inferior.

4. Single- versus multiple-nutrient particles. Although it was not conclusive, there was strong evidence of a beneficial effect on crop yields of having N, P, and K present in each particle of fertilizer as compared with dry mixtures of separate ingredients containing only one or two nutrient elements.

5. The nitric phosphate containing sulfur was definitely superior for cotton production in Alabama and Mississippi to the product without sulfur.

c. Ammoniated Superphosphate. A process for treatment of superphosphate with ammonia was first patented in 1873, but no commercial application appears to have been made of the idea until about 1930. Since the appearance of low-price ammonia in the United States, made possible by the expansion of domestic facilities for the production of synthetic nitrogen compounds, ammoniation has rapidly become standard practice among goods producers. The most recent estimate available (Anonymous, 1952) places the amount of nitrogen used in the United States for ammoniation of superphosphate during 1952 at 386,000 tons.

Beginning around 1928, extensive research on the chemical reactions and processing problems involved in ammoniation was begun, and Keenen (1930) published a report of the reactions that occur and the changes in composition of ordinary superphosphate (16 to 20 per cent P_2O_5) caused by ammoniation. Figure 5 taken from Keenen's paper and Fig. 6 taken from data of White *et al.* (1935) illustrate these changes for ordinary and concentrated superphosphate, respectively. Concentrated superphosphate, the simpler of the two superphosphates, is essentially monocalcium phosphate, and the first stage of neutralization of this acid phosphate with ammonia is the conversion of the monocalcium phosphate into the dicalcium salt and monoammonium phosphate. One mole of ammonia is required for each mole of water-soluble P_2O_5, or 0.12 part of NH_3 per part of water-soluble P_2O_5 in the superphosphate. Thus, a concentrated superphosphate containing 42 per cent water-soluble P_2O_5 would consume an amount of ammonia equal to about 5 per cent of the weight of the superphosphate during the first stage of neutralization. In the second stage of neutralization, dicalcium phosphate in the presence of water is converted into poorly defined basic calcium phosphates, perhaps amorphous in part, that simulate more or less closely the apatites. Because of the slight solubility of dicalcium phosphate, ammonia does not react with it as rapidly as with mono-

calcium phosphate; in fact, at the moisture levels customary in fertilizer practice, reaction is extremely slow at temperatures below 40° C. Accordingly, addition of ammonia normally causes premature formation of diammonium phosphate, which later may react slowly with the dicalcium phosphate in the fertilizer pile. Ammoniated concentrated

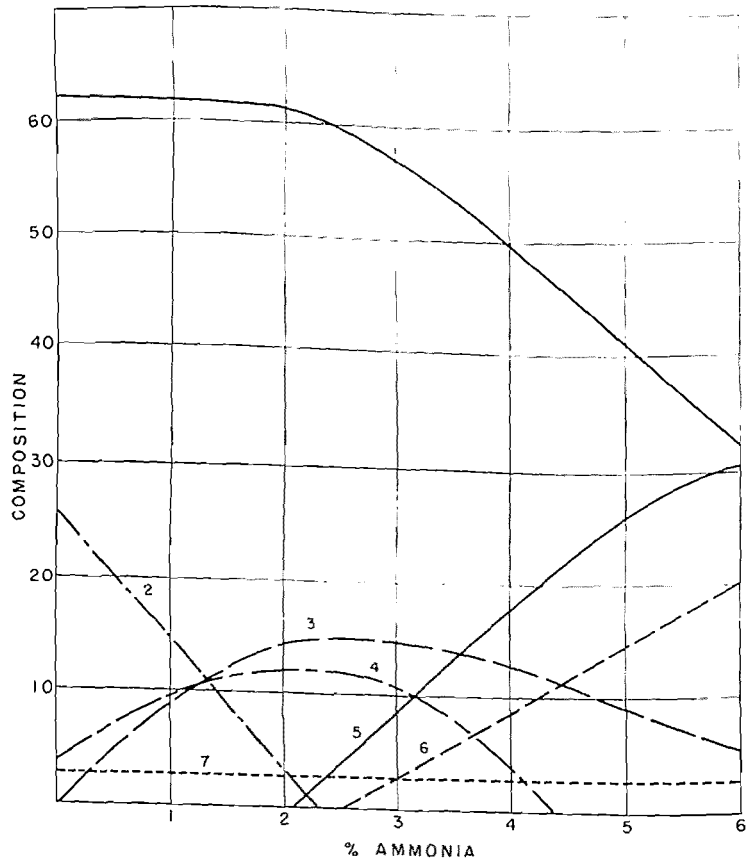


FIG. 5. Changes in composition of ordinary superphosphate caused by ammoniation (taken from Keenen, 1930). (1) Gypsum. (2) Monocalcium phosphate. (3) Monoammonium phosphate. (4) Dicalcium phosphate. (5) Precipitated tricalcium phosphate. (6) Ammonium sulfate. (7) Rock phosphate.

superphosphate containing up to nearly 14 per cent NH_3 has been prepared experimentally in a closed container by the addition of anhydrous ammonia to superphosphate (47 per cent water-soluble P_2O_5) at 100° C. Extensive formation of basic phosphate in the fresh material was not indicated below about 11 per cent ammonia. Even in highly ammoniated products water-soluble phosphorus is a principal constituent.

Ordinary superphosphate is essentially a mixture of monocalcium phosphate and calcium sulfate. The first stage of neutralization of

ordinary superphosphate is the same as that for concentrated superphosphate, but because of the lower phosphorus content the required amount of ammonia is less. For example, a superphosphate (20 per cent available P_2O_5) that contains 17.6 per cent water-soluble P_2O_5 would require about 2.1 per cent NH_3 for the first stage of neutralization. In

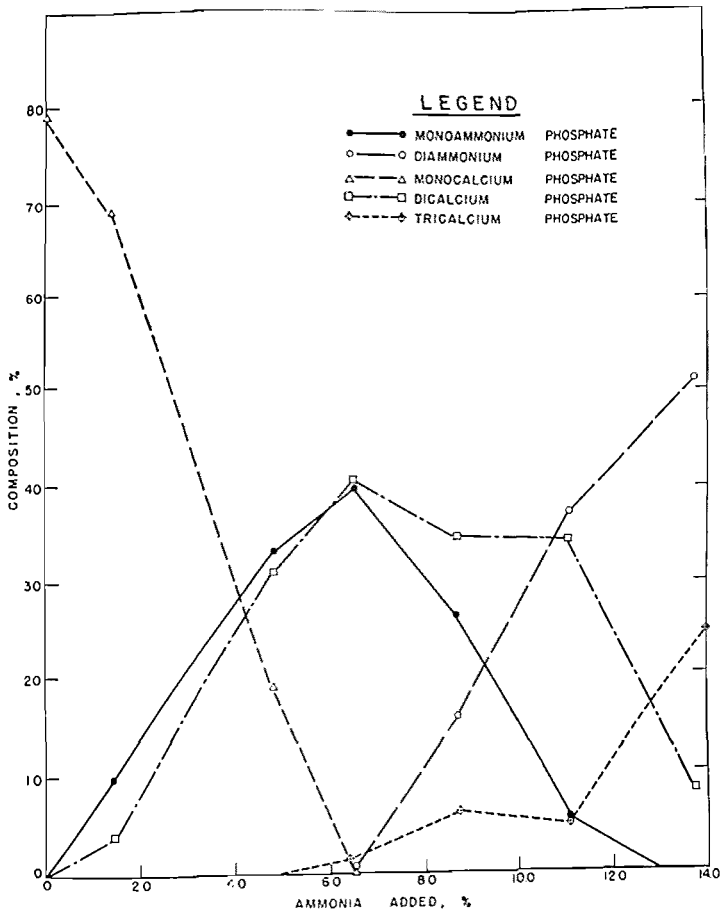


FIG. 6. Changes in composition of concentrated superphosphate caused by ammoniation (taken from White *et al.*, 1935).

the second stage of neutralization, dicalcium phosphate and calcium sulfate react with ammonia and monoammonium phosphate to form poorly defined basic phosphates and ammonium sulfate. The reaction runs more rapidly than that between dicalcium phosphate and ammonia, and, if sufficient calcium sulfate is present, the water-soluble phosphorus can be entirely eliminated by the addition of ammonia. This is the chief difference between ammoniated ordinary and concentrated superphosphates at very high ammoniation.

Among the advantages to ammoniation of superphosphate in the production of mixed fertilizers is the possibility of using the cheapest forms of nitrogen and producing a material of improved physical condition. The only disadvantage is the fact, already noted, that ammoniation much above 0.12 part of NH_3 per part of water-soluble P_2O_5 results in the formation of less-soluble compounds of phosphorus. Parker (1931) immediately recognized the possible importance of these changes from the agronomic standpoint and prepared a critical review of all the then known experimental results on the availability of the precipitated phosphates and of ammoniated superphosphate. These data indicated that the phosphorus in ammoniated superphosphate is from 75 to 100 per cent as effective as that in superphosphate. In 1935, Williamson (1935) published the results of the most extensive investigation that has yet been reported on the influence of ammoniation of superphosphate upon the nutrient value of the phosphorus. In this study 185 experiments were conducted on 12 different soil series in Alabama during the period 1931–1934. The data show that superphosphate ammoniated to 2 per cent N gave a *relative increase* of 100, but that when it was ammoniated to 4 per cent the *relative increase* fell to 85 compared to 100 as the increase from superphosphate. This work supported the observation of Ross *et al.* (1938) that including limestone to render the fertilizer mixture physiologically neutral increases the degree of reversion of phosphorus, when the mixture is ammoniated above 3 per cent. In the Alabama tests an average yield response of 53 pounds of seed cotton resulted from the use of 200 pounds of dolomite per acre mixed with nonammoniated superphosphate; when the dolomite was used with 4 per cent ammoniated superphosphate, however, the increase fell to only 16 pounds.

Among the sources studied by Salter and Barnes (1935) was superphosphate, ammoniated to three different levels (2.90, 5.36, and 7.12 per cent N) for greenhouse experiments and to two levels (2.5 and 5.0 per cent) for field experiments. The results of this investigation show that the effectiveness of these forms as sources of phosphorus varied with both the degree of ammoniation and the soil reaction. When compared to superphosphate, the materials ammoniated below 3 per cent showed relative nutrient values ranging from 72 to 100 per cent for soil reactions between pH 5.5 and 7.0. When they were ammoniated to 5 per cent, the value was lowered at all pH levels. Increasing the degree of ammoniation to 7 per cent decreased the effectiveness still further. Both of the two highly ammoniated materials showed consistently less nutrient value as the soil pH was increased up to 7.

The results described above have been, in general, substantiated by

later investigations by Andrews (1942) and Ross *et al.* (1947) and can be rationalized on the basis of composition of ammoniated ordinary superphosphate. According to Keenen (1930), the addition of 6 per cent of ammonia results in the formation of about 30 per cent tricalcium phosphate. The other forms of phosphorus present are presumed to be completely available to plants so that, under the most adverse conditions, the maximum loss of effectiveness that could result from ammoniation to this level would be less than 30 per cent.

An additional point of interest brought out by the work of Ross and co-workers (1947) is the fact that long-season crops are better able to utilize the phosphorus in highly ammoniated mixtures than are short-season crops. This is shown by the following data, taken from their report, on average *relative increases* in yield:

Degree of ammoniation, % NH_3	*Short-season crops*	*Long-season crops*
0	100	100
2	98	106
3	84	101
4	76	106
5	55	98

Millet, sorghum, and first cutting of Sudan grass were considered short-season crops. Wheat and second cutting of Sudan grass were considered long-season crops.

Very little attention seems to have been devoted to field tests of the effect of degree of ammoniation on availability of concentrated superphosphate. No serious effects would be expected, however, in view of the high proportion of available phosphorus compounds present, although a decrease in water-soluble phosphorus occurs. Rogers (1951), drawing on results obtained by a number of Southeastern States using nitric phosphates of different water-solubilities, concluded that there was no evidence on several crops for beneficial effect of water-soluble P_2O_5 above 10 per cent on the acid soils in this region. In the Western States, however, he found limited data indicating that materials having low water-soluble P_2O_5 are less effective on alkaline soils than are the phosphates with a high water-solubility.

As a result of repeatedly observed discrepancies between the availability of the phosphorus in ammoniated superphosphate as determined by approved chemical methods and as determined by plant growth, a series of studies of the nature and extent of the errors involved was sponsored by the Association of Official Agricultural Chemists during the period 1931–1944. Andrews (1942) summarized this situation and quoted field data from several Southern States in support of the need for

a second change in chemical methods for measuring available P_2O_5. The A.O.A.C. approved chemical method had been originally modified in 1932 to give higher results for available P_2O_5 in the ammoniated fertilizers primarily on the basis of results of tests of availability to crops of the individual components. Subsequently, it has been shown by Ross *et al.* (1947) that reactions occur during the ammoniation and storage of fertilizer mixtures that change the availability to plants of the phosphorus from that of the original component ammonium and calcium salts to a somewhat lower value. Results of the investigation reported by Ross and co-workers in 1947 showed that the presently approved A.O.A.C. chemical method gives high results for available P_2O_5 at levels of ammoniation above 2 per cent and that the error becomes greater as the degree of ammoniation is increased beyond that point.

In light of the general agreement among the results that have been reported it appears that the following general conclusions can be drawn: Ammoniation of ordinary superphosphate does not affect the availability to plants of the phosphorus up to an ammonia content of about 2 per cent. Addition of ammonia beyond that point results in a relatively small, though consistent, decrease in effectiveness as the percentage of ammonia is increased. The ammoniation of concentrated superphosphate to a given level results in a much smaller reversion of the phosphorus, but few reports of agronomic evaluation of these changes have been published.

III. Comparison of Materials Based on Absorption of Fertilizer Phosphorus, Using Tracer Technique

The efficiency of the various phosphorus sources as fertilizer materials has been discussed, up to this point, on the basis of crop yields as the criterion of effectiveness. Recently the development of the tracer technique has furnished another means of evaluation. The use of fertilizers tagged with radioactive phosphorus provides a sensitive method for distinguishing between the portion of the phosphorus in plants derived from the fertilizer and that derived from the native supply in the soil, and thus offers another method of evaluating the relative availability of the phosphorus in different materials.

Beginning in 1948 a cooperative radiophosphorus field experiment program was undertaken in the United States among a number of state experiment stations and the United States Department of Agriculture. All tagged fertilizers for this program were prepared by the U.S.D.A., thus insuring uniformity of materials. The tagged phosphates that have been produced and tested include ordinary and concentrated superphos-

phate, superphosphate ammoniated to different levels of nitrogen, tricalcium phosphate, dicalcium phosphate, calcium metaphosphate, ammonium phosphate, and nitric phosphates. These sources have been used in field and greenhouse studies under a variety of soil and climatic conditions, but most of the data have not been published. Studies reported by Hall (1949), Stanford and Nelson (1949), and Blaser and McAuliffe (1949) as well as the unpublished results of twenty-nine experiments carried out in eight states with five different crops grown on acid soils consistently show that as much or more phosphorus is absorbed from applied superphosphate as from any other source tested. Calcium metaphosphate tended to furnish more phosphorus to the plant than either di- or tricalcium phosphate, but in most cases somewhat less than superphosphate. On neutral to alkaline soils Dion *et al.* (1950) found that monoammonium phosphate supplied significantly larger amounts of phosphorus to wheat and barley than did monocalcium phosphate and that dicalcium phosphate was inferior to either of those sources. Olsen *et al.* (1950) also found that dicalcium phosphate furnished less phosphorus to wheat, barley, and sugar beets on calcareous soils than did superphosphate. Their results further showed that alfalfa and potatoes absorbed about equal amounts of phosphorus from calcium metaphosphate and from superphosphate. Tricalcium phosphate generally furnished less phosphorus to plants than did the other sources, although occasionally it furnished more than dicalcium.

Yield data were also recorded in the radiophosphorus experiments referred to above, but a yield response to applied phosphorus was found at only about one-third of the locations. As in the case of the earlier experiments cited in Table VIII, dicalcium phosphate and superphosphate were found to be equally effective on crop yields. On the basis of relative percentages of fertilizer phosphorus absorbed by the plant, however, the availability of the phosphorus in dicalcium phosphate averaged only 68 per cent as great as that in superphosphate. In these tests phosphorus availability apparently did not greatly affect the final yield.

It should be clearly recognized that the tagged atom technique simply provides another tool for use in studying some of the soil-fertilizer-plant relationships which are involved in the utilization of fertilizer phosphorus by plants. In the economic evaluation of phosphorus sources the final answer must be in terms of crop yields obtained on phosphorus-deficient soils when used at practical rates of application.

IV. Summary

Superphosphate, which has been the dominant form of phosphate fertilizer for more than a century, still tops the list of carriers in avail-

ability to plants for a wide range of soil, climate, and crop management conditions. Concentrated superphosphate has become the preferred standard for rating other sources of phosphorus because it does not contain sulfur, which under some conditions accounts in part for the responses obtained to ordinary superphosphate. The important commercial sources, semi-commercial, experimental, byproduct, and pure chemical forms of phosphate have been studied as sources of plant nutrient phosphorus. The various carriers when compared with superphosphate rate about as follows:

1. As a source of phosphorus, concentrated superphosphate is fully as effective on crop yields as ordinary superphosphate.

2. Granulation of fertilizers is a spreading practice primarily because of the improvement in physical condition which is accomplished. It has not been shown conclusively that there is any general agronomic value to granulation of superphosphate, although claims of crop responses to granulation have been noted.

3. The experimental data on raw mineral phosphates suggest these conclusions:

a. Many of the field experiments show that raw phosphates can be used with profit on acid soils that are deficient in phosphorus. In a majority of cases, however, superphosphate appeared to be a more economical source.

b. In tests where raw phosphates were most effective, from two to three times as much P_2O_5 was required in this form to give yield increases equal to those obtained from superphosphate.

c. The raw phosphates appear to differ somewhat in availability. In general, colloidal phosphate and rock phosphate give the same results when applied on an equivalent P_2O_5 basis.

d. Crops vary a great deal in their ability to feed on raw phosphates. Some of the legumes such as sweet clover, alfalfa, and red clover are strong feeders on raw phosphates, while nonlegumes, especially wheat, are not strong feeders. In general, short-season crops are not so responsive to raw phosphates as long-season and perennial crops.

e. Liming will decrease the effectiveness of raw phosphates, especially for crops that are not strong feeders. If legumes are grown in the rotation, only enough lime should be used to give optimum yields of the legumes. Raw phosphates are of little or no value when applied to calcareous soils.

f. Organic matter appears to have little or no solvent action on raw phosphates. Heavy applications of manure may appear to in-

crease the effectiveness of phosphates by lessening the need for additional phosphorus.

g. Where raw phosphates have shown better residual value than superphosphate, the raw phosphates were applied at much higher rates of P_2O_5.

4. Mono-, di-, and tricalcium phosphate rank in the order named in effectiveness on alkaline or calcareous soil. On the basis of crop yields, however, dicalcium phosphate is fully as effective as a source of phosphorus as is monocalcium phosphate or superphosphate on acid to neutral soils. Tricalcium, on the other hand, is less effective than either the mono- or dicalcium salts.

5. Fused tricalcium phosphate, when ground to pass a 40-mesh sieve, compares favorably with superphosphate as a source of phosphorus for white clover-grass mixtures on the acid soils of the Southeastern United States. On the other hand, this product has given *relative increase* values of 92 on small grain as an average of 33 locations, 95 on corn at 46 locations, and 86 on cotton at 13 locations. Tests on alkaline or calcareous soils show conclusively that this is not a satisfactory source for these conditions. Calcined phosphates have performed similarly to fused tricalcium phosphate when materials of approximately the same fineness were compared.

6. The metaphosphates are generally satisfactory as sources of phosphorus on the more important agricultural soils of the humid region. Calcium metaphosphate is not so dependable a source of phosphorus for alkaline soils as the water-soluble phosphates, although more favorable results have been obtained with it on calcareous soils than with di- or tricalcium phosphates.

7. Basic slag has been more effective as a source of phosphorus for corn, winter legumes, and pastures than for cotton and small grain. For the latter crops this product has produced yield increases ranging between 83 and 95 per cent of the increase obtained with superphosphate.

8. Bone meal has been less effective on heavily limed soils and has ranged in value from about 80 to 98 per cent as effective in increasing yields of crops as superphosphate on more-acid soils.

9. Rhenania or silicophosphate was as effective as superphosphate on root crops such as swedes and potatoes in tests in Great Britain on soil with pH less than 5.5. On less-acid and neutral soils, superphosphate was superior.

10. Rock phosphate-magnesium silicate glass has been found to be an unsatisfactory source of phosphorus on alkaline soils or for quick-

growing vegetable crops on moderately acid to neutral soils of the Northwest.

11. Liquid phosphoric acid, sodium and potassium phosphates, and a large group of miscellaneous inorganic phosphates appear to be good sources of plant nutrient phosphorus.

12. Most of the organic phosphates tested appear to be about as available to plants when added to soils as monocalcium phosphate. Triethyl, tricresyl, and triphenyl phosphates are exceptions.

13. The ammonium phosphates are well adapted to alkaline soils and are good sources of phosphorus on acid soils when their residual acidity is neutralized with limestone.

14. The phosphorus in the nitric phosphates appears to be as effective as superphosphate for corn, cotton, and small grain on acid soils of the humid regions.

15. Ammoniation of ordinary superphosphate, up to a nitrogen content of about 2 per cent, does not affect the availability of the phosphorus to plants. Additional ammoniation produces a small but consistent decrease in phosphorus availability. Ammoniation of concentrated superphosphate to a given level results in much smaller reversion of the phosphate.

16. Absorption data obtained by use of the tracer technique have rated several of the phosphates as follows: Superphosphate = ammonium phosphate > calcium metaphosphate > dicalcium phosphate > tricalcium phosphate. Marked differences in the availability of superphosphate and dicalcium phosphate as expressed in percentage of fertilizer phosphorus absorbed by plants have not been reflected in crop yields.

REFERENCES

ALLISON, FRANKLIN E., PINCK, L. A., and SHERMAN, MILDRED S. 1941. Comparative availabilities of organic and inorganic phosphates as shown by the Neubauer method. *J. Am. Soc. Agron.* **33**: 918–926.

ALWAY, F. J., and NESOM, G. H. 1944. Effectiveness of calcium metaphosphate and fused rock phosphate on alfalfa. *J. Am. Soc. Agron.* **36**: 73–88.

ANDREWS, W. B. 1942. Discrepancies between the response of cotton to phosphatic materials and their availability as determined by the official method. *J. Assoc. Offic. Agr. Chemists* **25**(2): 498–509.

ANONYMOUS. 1952. The fertilizer situation for 1951–52. Production and Marketing Administration, United States Department of Agriculture, Washington, D. C., February, 1952.

ANTHONY, J. L. 1952. The response of crops to applied phosphate on some Mississippi soils. *Proc. Assoc. Southern Agr. Workers*, p. 47.

ARMIGER, W. H., HILL, W L., PINKERTON, CECIL, LAKIN, H. W., and ROBINSON, W. O. 1947. Composition and fertilizer value of spent phosphate catalysts from the pertoleum industry: "Solid phosphoric acid catalysts" and copper pyrophosphate catalysts. *J. Am. Soc. Agron.* **39**: 318–326.

BARTHOLOMEW, R. P. 1928. The unavailability of phosphorus in rock phosphate to some southern crops. *J. Am. Soc. Agron.* **20**: 913–920.

BARTHOLOMEW, R. P. 1935. Fluorine, its effect on plant growth and its relation to the availability to plants of phosphorus in phosphate rock. *Soil Sci.* **40**: 203–217.

BARTHOLOMEW, R. P. 1950. Crop rotation and fertilization for soil improvement. *Arkansas Agr. Expt. Sta. Bull.* **497**.

BAUER, F. C. 1921. The relation of organic matter and feeding power of plants to the utilization of rock phosphate. *Soil Sci.* **12**: 12–41.

BAUER, F. C., LANG, A. L., BADGER, C. J., MILLER, L. B., FARNHAM, C. H., JOHNSON, P. E., MARRIOTT, L. F., and NELSON. M. H. 1945. Effects of soil treatment on soil productivity. *Illinois Agr. Expt. Sta. Bull.* **516**.

BEREZOVA, E., and FODEEVA, A. 1950. The nature of the effect of granulated superphosphate. *Agrobiologia.* **1**: 89–95.

BLASER, R. E., VOLK, G. M., and SMITH, F. B. 1941. The yield, composition and nodulation of several clover varieties as affected by sources of calcium and phosphorus in combination with other fertilizers on several soils. *Soil Sci. Soc. Amer. Proc.* **6**: 298–302.

BLASER, R. E., and MCAULIFFE, CLAYTON. 1949. Utilization of phosphorus from various fertilizer materials: I. Orchard grass and Ladino clover in New York. *Soil Sci.* **68**: 145–150.

BLEDSOE, R. P. 1929. Cotton fertilizers and cultural methods. *Georgia Agr. Expt. Sta. Bull.* **152**.

BRAY, R. H. 1937. Phosphorus availaibility and crop response. *Soil Sci. Soc. Amer. Proc.* **11**: 215–221.

BROWN, B. E., CHUCKA, J. A., HAWKINS, A., and CAMPBELL, J. E. 1944. Field comparisons of colloidal phosphate and superphosphate as sources of phosphorus in potato fertilizers. *Am. Potato J.* **21**: 241–249.

BROWN, B. E., and HAWKINS, A. 1944. A comparison of colloidal phosphate, rock phosphate, and superphosphate as sources of phosphorus in potato fertilizer in Aroostock County, Maine. *Am. Fertilizer* **100**(8): 5–7, 26.

BROWN, B. E., and JACOB, K. D. 1944. Greenhouse and field tests comparing colloidal phosphate, phosphate rock and superphosphate as sources of phosphorus for various crop plants. *Am. Fertilizer* **101** (13): 7–10, 22, 24, 26, 28, 30.

BROWN, B. E., CAMPBELL, J. C., HAWKINS, A., HOUGHLAND, G. V. C., and JACOB, K. D. 1943. An evaluation of sludge-acid and alkylation-acid superphosphates as sources of phosphorus in potato fertilizers *Am. Potato J.* **20**: 89–95.

BROWN, B. E., and CLARK, D. G. 1943. An appraisal of calcium and potassium metaphosphates as sources of phosphorus for crop plants. *Am. Fertilizer* **95**(5): 10–11, 24, 26.

BURLISON, W. L. 1916. Availability of mineral phosphates for plant nutrition. *J. Agr. Research* **6**(13): 485–514.

CHANDLER, R. F., and MUSGRAVE, R. B. 1944. A comparison of potassium chloride and potassium metaphosphate as sources of potassium for plants. *Soil Sci. Soc. Amer. Proc.* **9**: 151–153.

CONNER, S. C., and ADAMS, J. E. 1926. Availability of Tennessee raw rock phosphate in relation to fineness and other factors. *J. Am. Soc. Agron.* **18**: 1103–1107.

CONVERSE, CHARLES D. 1948. Phosphorus fertility and movement studies on newly reclaimed sandy soil. *Soil Sci. Soc. Amer. Proc.* **13**: 423–427.

CROWTHER, E. M., and COOKE, G. W. 1951. The production and agricultural value of silicophosphate fertilizers. Part VI. Field experiments. Monograph No. 11. 108, pp. 210–243. Ministry of Supply, London.

CROWTHER, E. M., and LEA, F. M. 1946. Silico phosphate. *J. Am. Soc. Agron.* 53(3): 102–103.

DAVIS, F. L. 1937. Granulated versus pulverized fertilizer for cotton on Olivier silt loam. *Proc. Natl. Joint Comm. Fertilizer Application, 13th Ann. Meeting*, p. 72.

DETURK, E. E. 1926. *39th Ann. Rep. Illinois Agr. Expt. Sta.*, p. 23.

DETURK, E. E. 1942. The problem of phosphate fertilizers. *Illinois Agr. Expt. Sta. Bull.* **484.**

DICKMAN, S. R., and DETURK, E. E. 1940. Response of young corn plants to inorganic phosphate differing in solubility: 1. The effect of phosphorus absorption from rock phosphate on the composition and dry weight of corn at three periods. *Soil Sci. Soc. Amer. Proc.*, **5**: 213–219.

DION, H. G., DEHM, J. E., and SPINKS, J. W. T. 1950. Tracer studies with phosphate fertilizers. *Canadian Chem. and Process. Inds.*, November, pp. 1–7.

ENSMINGER, L. E. 1950. Response of crops to various phosphate fertilizers. *Alabama Agr. Expt. Sta. Bull.* **270.**

ENSMINGER, L. E., and COPE, J. T., JR. 1947. Effect of soil reaction on the efficiency of various phosphates for cotton and on loss of phosphorus by erosion. *J. Am. Soc. Agron.* **39**: 1–11.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1951. Fertilizers—a world report on production and consumption, p. 5.

FRANCK, O. 1948. Forsok Med. Nedmyllming av handelsgjodsel. *LantbrHögsk. JordbrFörsökanst. Medd.* **26**, p. 26.

FUDGE, J. F., and FRAPS, G. S. 1945. The value of different phosphates for various Texas soils and grasses as indicated by pot experiments. *Texas Agr. Expt. Sta. Bull.* **672.**

GAROLA, J. 1951. Action comparée de l'acide phosphorique sans forms de super phosphate pulverulent et granule. Bull. Document **9**: 10–13. (F.E.).

GRANTHAM, G. M., and HOUGHLAND, G. V. C. 1937. Fertilizer placement studies with potatoes in Michigan—season of 1937. *Proc. Natl. Joint Comm. Fertilizer Application, 13th Ann. Meeting, pp.* 87–90.

GREEN, J. 1938. Phosphate investigations in Montana—1937. *Montana Agr. Expt. Sta. Bull.* **356.**

GRIFFITHS, A. E., and FINCH, A. H. 1945. Further studies on the response of lettuce to fertilization. *Arizona Agr. Expt. Sta. Bull.* **199.**

HALL, N. S., NELSON, W. L., KRANTZ, B. A., WELCH, C. D., and DEAN, L. A. 1949. Utilization of phosphorus from various fertilizer materials: II. Cotton and corn in North Carolina. *Soil Sci.* **68**: 151–156.

HARDESTY, J. O., and CLARK, K. G. 1951. Granulation of fertilizers. *Agr. Chemicals* **6**: 34–38, 95, 97.

HARTWELL, BURT L., and DAMON, S. C. 1927. The degree of the response of different crops to various phosphorus carriers. *Rhode Island Agr. Expt. Sta. Bull.* **209.**

HENDRICKS, S B., HILL, W. L., JACOB, K. D., and JEFFERSON, M. E. 1931. Structural characteristics of apatite-like substances and composition of phosphate rock as determined from microscopical and X-ray diffraction examinations. *Ind. Eng. Chem.* **23**: 1413–1418.

HIGNETT, T. P. 1951. Nitric acidulation of rock phosphate. *Chem. Eng.* **58**: 166–169.

HILL, W. L., WARD, F. N., ARMIGER, W. H., and JACOB, K. D. 1948. Composition and fertilizer value of phosphate rock—magnesium silicate glasses. *J. Assoc. Offic. Agr. Chemists* **31**: 381–397.

HINKLE, D. A. 1942a. Efficiency of various phosphate fertilizers on calcareous soils for alfalfa and sweet clover. *J. Am. Soc. Agron.* **34**: 913–918.

HINKLE, D. A. 1942b. Use of phosphatic fertilizers on alfalfa. *New Mexico Agr. Expt. Sta. Bull.* **289**.

HOLMBERG, D. M., LORENZ, O. A., and ZOBEL, M. P. 1944–1949. Fertilizer trials on vegetables in Yolo County. *Calif. Agr. Ext. Ser.* (mimeographed).

HONKAVAARA, T. 1951. Effects de la granulation et du semis en lignes sur l'efficacité des engrais phosphates. *Bull. Document Assoc. Internat. des Fabricants de Superphos.* **10**: 17–25.

HOPKINS, C. G. 1916. Phosphates and honesty. *Illinois Agr. Expt. Sta. Circ.* **186**.

HOUGHLAND, G. V. C., CLARK, K. G., HAWKINS, A., and CAMPBELL, JOHN C. 1942. Nutrient value of some new phosphatic materials used on potatoes. *Am. Fertilizer* **97**(7): 5–8, 24, 26.

IDAHO AGRICULTURAL EXPERIMENT STATION. 1943. Comparative values of various phosphate carriers determined. *Idaho Agr. Expt. Sta. Bull.* **251**: 9–10.

IOWA AGRICULTURAL EXPERIMENT STATION. 1947. First Annual Report of Western Iowa Experimental Farm.

JACOB, K. D. 1944. A review of experiments relating to the fertilizing value of defluorinated phosphate rock. *U. S. Dept. Agr. Spec. Rept.* **9**.

JACOB, K. D. 1951. Processes and facilities for manufacture of phosphate fertilizers in the United States. *Com. Fertilizer* **82**(2): 20–22, 24, 26, 27, 29, 30–31, 34, 38.

JACOB, K. D., HILL, W. L., MARSHALL, H. L., and REYNOLDS, D. S. 1933. The composition and distribution of phosphate rock with special references to the United States. *U. S. Dept. Agr. Tech. Bull.* **364**.

JACOB, K. D., BARTHOLOMEW, R. P., BROWN, B. E., PIERRE, W. H., REID, F. R., and TIDMORE, J. W. 1935. Nutrient value of phosphorus in calcined phosphate as determined by growth of plants in greenhouse experiments. *J. Agr. Research* **50**: 837–48.

JACOB, K. D., and ROSS, WILLIAM H. 1940. Nutrient value of the phosphorus in defluorinated phosphate, calcium metaphosphate, and other phosphatic materials as determined by growth of plants in pot experiments. *J. Agr. Research* **61**(7): 539–560.

JACOB, K. D., and ARMIGER, W. H. 1944. Field experiments with alkylation-acid superphosphate. *J. Am. Soc. Agron.* **36**: 281–286.

JONES, RANDALL J., and ROGERS, HOWARD T. 1949. New fertilizers and fertilizer practices. *Advances in Agron.* **1**: 39–76.

KARRAKER, P. E., MILLER, HAROLD F., BORTNER, C. E., and TODD, J. R. 1941. Greenhouse tests of the availability of phosphorus in certain phosphate fertilizers. *Kentucky Agr. Expt. Sta. Bull.* **413**: 59–86.

KEENEN, FRANK G. 1930. Reactions occurring during the ammoniation of superphosphate. *Ind. Eng. Chem.* **22**: 1378–1387.

KENTUCKY AGRICULTURAL EXPERIMENT STATION. 1950. Summary of results of experiments at Western Kentucky Substation, 1927–1949.

LARSEN, L. 1951. Experences au champ avec superphosphate granule appliqué au semoir et a la volée. *Bull. Document. Assoc. Internat. des Fabricants de Superphos* **9**: 5–6. (F.E.).

LARSON, H. W. E., and BAKER, G. O. 1939. A preliminary report on the relative value of various phosphate fertilizers for southern Idaho soil conditions. *Idaho Ext. Bull.* **120**.

LONG, O. H., and WINTERS, ERIC. 1951. Fused tricalcium phosphate. *Tennessee Ag Expt. Sta. Circ.* **107**.

LYON, T. L. 1933. A test of floats as fertilizer and a study of the influence of farm manure on their effectiveness. *New York Agr. Expt. Sta. Bull.* **574.**

LYZIN, D. A. 1951. The effectiveness of granular fertilizer on chernozems of the Southeastern SRR. *Sovet. Agron.* **10**(1): 27–32.

MACINTIRE, W. H., WINTERBERG, S. H., HARDIN, L. J., STERGES, A. J., and CLEMENTS, L. B. 1948. Analytical evaluation of certain synthetic organic phosphates in relation to their fertilizer effectiveness in pot cultures. *Soil Sci.* **66**: 249–258.

MACINTIRE, W. H., WINTERBERG, S. H., HARDIN, L. J., STERGES, A. J., and CLEMENTS, L. B. 1950. Fertilizer evaluation of certain phosphorus and phosphoric materials by means of pot cultures. *Agron. J.* **42**: 543–549.

MCGEORGE, W. T. 1939. Factors influencing the availability of native soil phosphate and phosphate fertilizers in Arizona soils. *Univ. Ariz. Tech. Bull.* **82.**

MEHRING, A. L. 1944. Double superphosphate. *U. S. Dept. Agr. Circ.* **718.**

MEHRING, A. L. 1948. Fertilizer consumption and supply in the North Central States. *Better Crops with Plant Food* **32**(5): 6–14, 40–47.

MEHRING, A. L. 1953. *In* Fertilizer Technology in the United States. Agronomy Monograph, Vol. 3. Academic Press, New York.

MEHRING, A. L., WHITE, L. M., ROSS, W. H., and ADAMS, J. E. 1935. Effects of particle size on efficiency of fertilizers. *U. S. Dept. Agr. Tech. Bull.* **485.**

MERRILL, L. H. 1891. Ability of different plants to get phosphoric acid from crude phosphates. *Maine Agr. Expt. Sta. 7th Ann. Rept.* 123–144.

MIDGLEY, ALVIN R., and DUNKLEE, DAVID E. 1945. The availability to plants of phosphates applied with cattle manure. *Vermont Agr. Expt. Bull.* **525.**

MILLER, HAROLD. 1952. Calcium metaphosphate and fused tricalcium phosphate. *Kentucky Agr. Expt. Sta.* (mimeographed).

MITCHELL, J., DEHM, J. E., and DION, H. G. 1952. The effect of small additions of elemental sulfur on the availability of phosphate fertilizer. *Sci. Agr.* **32**: 311–16.

MOOERS, C. A. 1929. The comparative values of different phosphates. *Tennessee Agr. Expt. Sta. Bull.* **141.**

NELLER, J. R. 1945. Availability of the phosphorus of various types of phosphates added to Everglades peat land. *Florida Agr. Expt. Sta. Bull.* **408.**

NELLER, J. R., KILLINGER, G. B., JONES, D. W., BLEDSOE, R. W., and LUNDY, H. W. 1951. Sulfur requirement of soils for clover-grass pastures in relation to fertilizer phosphates. *Florida Agr. Expt. Sta. Bull.* **475.**

NOLL, C. F., and IRVIN, C. J. 1942. Field test of phosphate fertilizers. *Pennsylvania Agr. Expt. Sta. Bull.* **423.**

NORDENGREN, S. 1948. Granulation of phosphatic fertilizer—theory and practice. *Fertiliser Society Papers.* London.

O'BRIEN, R. E. 1944. Field experiments with phosphatic fertilizers. *Virginia Agr. Expt. Sta. Bull.* **364.**

ODLAND, T. E., and COX, T. R. 1942. Field experiments with phosphate fertilizer. *Rhode Island Agr. Expt. Sta. Bull.* 281.

OLSEN, S. R., SCHMEHL, W. R., WATANABA, FRANK S., SCOTT, C. O., FULLER, W. H., JORDAN, J. V., and KUNKEL, ROBERT. 1950. Utilization of phosphorus by various crops as affected by source of material and placement. *Colorado Agr. Expt. Sta. Bull.* **42.**

PAAUW, F. 1950. Oorzaken van de verschielende werking van superfosfaat en Thomasslakkenmeel. *Verslag. Landbouwk. Onderzoek.* **56**(6): 94.

PARKER, F. W. 1931. The availability of phosphoric acid in precipitated phosphates. *Com. Fertilizer* **42**(5): 28–44.

PINCK, L. A., SHERMAN, MILDRED S., and ALLISON, F. E. 1941. The behavior of soluble organic phosphates added to soils. *Soil Sci.* **51**: 351–365.

PITTMAN, D. W., and THORNE, D. W. 1941. Fertilizers for Utah soils. *Utah Agr. Expt. Sta. Circ.* **116**.

RICH, C. I., and LUTZ, J. A. 1950. Crop response to phosphate fertilizer in Virginia. *Virginia Agr. Expt. Sta. Tech. Bull.* **115**.

ROBERTS, GEORGE, FREEMAN, J. F., and KINNEY, E. J. 1939. Soil management experiments. *Univ. Kentucky Bull.* **397**.

ROBERTS, GEORGE, FREEMAN, J. F., and MILLER, HAROLD. 1942. Field tests of the relative effectiveness of different phosphate fertilizers. *Kentucky Agr. Expt. Sta. Bull.* **420**.

ROGERS, HOWARD T. 1951. Crop response to nitraphosphate fertilizers. *Agron. J.* **43**: 468–476.

ROGERS, H. T., PEARSON, R. W., and PIERRE, W. H. 1940. Absorption of organic phosphorus by corn and tomato plants and the mineralizing action of exoenzyme systems of growing roots. *Soil Sci. Soc. Amer. Proc.* **5**: 285–291.

ROSS, W. H., ADAMS, J. RICHARD, HARDESTY, JOHN O., and WHITTAKER, COLIN. 1947. Factors affecting the availability of ammoniated superphosphates: II. The efficiency of ammoniated superphosphates as indicated by pot tests in the greenhouse. *J. Assoc. Offic. Agr. Chemists.* **30**: 624–640.

ROSS, W. H., and JACOB, K. D. 1937. Report on phosphoric acid. Availability of calcined phosphate and other new phosphatic materials as determined by chemical and vegetative tests. *J. Assoc. Offic. Agr. Chemists*, **20**: 231–249.

ROSS, W. H., RADER, L. F. JR., and BEESON, K. C. 1938. Citrate-insoluble phosphoric acid in ammoniated mixtures containing dolomite. *J. Assoc. Offic. Agr. Chemists* **21**(2): 258–268.

RUSSELL, E. J., and GARNER, H. V. 1941. Rothamsted experiments on the manuring of potatoes. II. Effects of inorganic and organic manures on yields of potatoes. *Empire J. Exptl. Agr.* **9**: 217–226.

SALTER, ROBT. M. 1936. Granular versus ordinary fertilizer. *Proc. Natl. Joint Comm. Fertilizer Application, 12th Ann. Meeting*, pp. 87–90.

SALTER, ROBT. M., and BARNES, E. E. 1935. The efficiency of soil and fertilizer phosphorus as affected by soil reaction. *Ohio Agr. Expt. Sta. Bull.* **553**.

SAYRE, C. B. 1936. Granulated fertilizers. *Proc. Natl. Joint Comm. Fertilizer Application, 12th Ann. Meeting*, pp. 117–120.

SCHARRER, K. 1950. Arbeiten uber Rhenania-Phosphat in Weihenstephan und Giessen. *Z. Pflanzenernähr Düng. Bodenk.* **50**: 236–246.

SCHOLL, W., and WALLACE, H. M. 1952. Commercial fertilizers—consumption in the United States 1950–1951. *Com. Fertilizer* **84**(6): 20–21, 24–25, 28–29, 34, 36, 40–41.

SKINNER, J. G., MCKAIG, NELSON, JR., HARDESTY, J. O., COLLINS, E. R., KILLINGER, G. B., and STACY, S. V. 1941. Effectiveness on cotton soils of granulated mixed fertilizers of different particle size. *J. Am. Soc. Agron.* **33**: 314–324.

SMITH, G. E. 1942. Sanborn Field—fifty years of field experiments with crop rotations, manure and fertilizers. *Missouri Agr. Expt. Sta. Bull.* **458**.

SPENCER, V. E., and STEWART, ROBERT. 1934. Phosphate studies: I. Soil penetration of some organic and inorganic phosphate. *Soil Sci.* **38**: 65–79.

STANFORD, GEORGE, and NELSON, L. B. 1949. Utilization of phosphorus from various fertilizer materials: III. Oats and alfalfa in Iowa. *Soil Sci.* **68**: 157–161.

TENNESSEE VALLEY AUTHORITY. 1946. The approach to agricultural development in the Tennessee Valley. *Soil Sci. Soc. Amer. Proc.* **11**: 369–373.

TERMAN, GILBERT L. 1944. Effectiveness of fused phosphate of different particle size. *Soil Sci. Soc. Amer. Proc.* **9**: 154–158.

THORNE, D. W. 1944. The use of acidifying materials on calcareous soils. *J. Am. Soc. Agron.* **36**: 815–828.

THORNE, C. E. 1916. Raw phosphate rock as a fertilizer. *Ohio Agr. Expt. Sta. Bull.* **305.**

TOEVS, JOHN L., and BAKER, G. ORIEN. 1939. Progress report of phosphate and other fertilizer investigations at the Aberdeen Branch Station. *Idaho Agr. Expt. Sta. Bull.* **230.**

TREMBLAY, F. T., and BAUR, K. E. 1952. The effect of solubility of phosphate fertilizers on the yield of vegetable crops. Paper presented before the American Chemical Society meeting in Atlantic City, New Jersey.

TRUOG, E. 1912. Factors influencing the availability of rock phosphate. *Wisconsin Agr. Expt. Sta. Bull.* **20.**

TRUOG, E. 1916. The utilization of phosphates by agricultural crops, including a new theory regarding the feeding power of plants. *Wisconsin Agr. Expt. Sta. Research Bull.* **41.**

VISHINSKY, A. M. 1950. The effect of granular fertilizers on yields of grain crops and sugar beets. *Sovet. Agron.* **8**: 18–25.

VLASIUK, P. A. 1950. Granulation—a method of increasing the effectiveness of fertilizers. *Agrobiologia* **4**: 143–154.

VOLK, GARTH W. 1942. Waste pond phosphate compared with rock phosphate and superphosphate as a fertilizer. *J. Am. Soc. Agron.* **34**: 823–829.

VOLK, GARTH W. 1944. Availability of rock and other phosphate fertilizers as influenced by lime and form of nitrogen fertilizer. *J. Am. Soc. Agron.* **36**: 46–56.

VOLKERDING, C. C., and STOA, T. E. 1947. Is rock phosphate a good fertilizer for North Dakota? *North Dakota Agr. Expt. Sta. Bimonthly Bull.* **10**(1): 13–17.

WEEKS, M. E., and MILLER, H. F. 1948. The residual effects of phosphates used on long-time field experiments. *Soil Sci. Soc. Amer. Proc.* **13**: 102–107.

WEISER, V. L. 1933. Fixation and penetration of phosphates in Vermont soils. *Vermont Agr. Expt. Sta. Bull.* **356.**

WHITE, L. M., HARDESTY, J. O., and ROSS, W. H. 1935. Ammoniation of double superphosphate. *Ind. Eng. Chem.* **27**: 562–567.

WIANCKO, A. T., and CONNER, S. D. 1916. Acid phosphate vs. raw rock phosphate as fertilizer. *Indiana Agr. Expt. Sta. Bull.* **187.**

WILLIAMS, E. G., and REITH, J. W. S. 1948. The relative effectiveness of phosphatic fertilizers. *Empire J. Expt. Agr.* **16**: 1–13.

WILLIAMSON, J. T. 1935. Efficiency of ammoniated superphosphates for cotton. *J. Am. Soc. Agron.* **27**: 724–728.

WILLIS, W. P., JR., and HARRINGTON, F. M. 1939. Phosphate investigations in Montana—1938. *Montana Agr. Expt. Sta. Bull.* **369.**

WOODHOUSE, W. W., JR. 1945. Use of T. V. A. phosphates and limestone on permanent pastures. *North Carolina Agr. Expt. Sta. and T. V. A. Circ.* **140.**

WOODHOUSE, W. W., JR. 1949. Comparisons of rock phosphate and superphosphate on crop yields. A summary of data. *North Carolina Agr. Expt. Sta. Circ.* **148.**

CHAPTER VIII

Soil Management Practices in Relation to Phosphorus Availability and Use

GEORGE STANFORD and W. H. PIERRE

I. Introduction

In the broadest sense it may be said that most soil management practices affect, either directly or indirectly, the utilization of phosphorus by plants and the efficient use of phosphorus fertilizers. For purposes of this discussion, the more important of these practices can be grouped into two general categories. First, there are those that influence directly the availability of native or applied phosphorus. Among these, the ones that have been more fully recognized and investigated are: (a) liming, (b) the application of manures and crop residues, (c) the rate, time, and frequency of phosphorus applications, (d) the placement of the fertilizer, and (e) cropping and erosion control practices. Secondly, there are those practices that do not affect phosphorus availability directly but affect the need of the crop for phosphorus and its ability to get phosphorus from the soil. Among these are: (a) the application and availability of other nutrients, (b) the crops grown in the rotation, and (c) irrigation and drainage, as they affect not only total growth and needs but also root distribution.

This grouping is to some extent arbitrary, since the practices in the two groups are neither mutually exclusive nor unrelated. Liming, manuring, and fertilization, for example, supply other nutrients and, therefore, indirectly affect the need and utilization of phosphorus by plants. Conversely, drainage and irrigation not only affect phosphate availability indirectly, but also, by influencing aeration and moisture supply, alter the chemical and positional availability of native and applied phosphates.

This discussion will be limited primarily to the practices in the first group that are not discussed specifically by other contributors to this symposium. Liming is discussed in Chapter IX, and cropping and erosion control practices in Chapter XIV. Neither will any attempt be made to discuss the various factors affecting phosphorus availability

except as they relate to specific practices, since these factors are discussed in earlier chapters (Chapters II, III, IV, and V). Special attention will be given, however, to the relation of subsoil phosphorus to the efficient use of fertilizers and to practices that may be effective in increasing the availability of phosphorus in subsurface or subsoil horizons.

II. Additions of Organic Materials

1. Phosphorus Supplied by Organic Materials

The phosphorus nutrition of plants is influenced in various ways by the addition of organic materials to the soil. The phosphorus directly contributed through green manures, crop residues, and farm manure, as well as the direct or indirect effects of these materials upon the availability of phosphorus applied in commercial fertilizers or present in the soil, merit special consideration in a discussion of soil management practices affecting phosphorus use.

The problem of predicting the behavior of phosphorus returned to the soil in organic materials is complicated by several factors. The relative rates of immobilization of inorganic phosphorus and mineralization of organic forms undoubtedly exert considerable influence on the amount of phosphorus available to the plant at various stages of decomposition of the added materials. As pointed out in Chapter V the net effect of these opposing microbiological transformations is determined, to a considerable extent, by the amount and nature of the phosphorus in the materials, the carbon:phosphorus ratio, the carbon:nitrogen ratio, and the nature of the carbon constituents, as well as by various environmental factors. A further complication is that microbial activity may enhance the rate of release of phosphorus from native or residual forms of phosphorus in soils.

Recent developments with the use of radiophosphorus have opened new avenues of approach to this important problem. Using radiophosphorus, certain investigators have been successful in determining the amount of phosphorus which is directly contributed to growing plants by added plant materials or farmyard manure, as distinct from that which is supplied by the soil itself. Moreover, the possibility of gaining a more thorough understanding of some of the indirect effects of organic matter additions upon the availability of applied as well as native forms of phosphorus, has been clearly indicated in certain of these investigations.

a. Green Manures and Crop Residues. Through the use of plant material containing phosphorus tagged with P^{32}, certain investigators recently have found that the availability of phosphorus in certain plant

materials may compare favorably with that of superphosphate. Fuller and Dean (1949) found that the green manure phosphorus from wheat tops and roots was about 70 per cent as efficient as superphosphate where these materials were mixed with the soil under greenhouse conditions. Where the plant material was placed in layers to simulate field application, the per cent utilization of phosphorus exceeded that from superphosphate applied on an equivalent phosphorus basis. More recently Fuller and Rogers (1951) found that, as a source of phosphorus to rye grass on calcareous soils, barley straw was better than superphosphate. Likewise, White, Fried, and Ohlrogge (1949) found that alfalfa was as effective as potassium dihydrogen phosphate during a 5-week period following incorporation of the green manure. Nielsen (1952), on the other hand, found that a somewhat lower percentage of the phosphorus applied in ground alfalfa green manure was taken up by corn plants than from the fertilizer.

As stated earlier, there are several factors which may influence the rate at which phosphorus in added plant materials is made available to the crop. The proportion of phosphorus present in the inorganic form undoubtedly is of importance. The content of inorganic phosphorus in plant materials may be relatively high as, for example, in the studies of Fuller and Dean (1949) and Fuller and Rogers (1951), where 50 to 70 per cent of the phosphorus occurred in inorganic form. This phosphorus fraction would be expected to be equally as available to plants as that supplied in superphosphate. In fact, there is some evidence (see Section II.2.b) that the inorganic plant phosphorus would be fixed to a lesser extent, because of the influence of the intimately associated organic material, than that added in the fertilizer.

Still another aspect of the problem concerns the effect on phosphorus availabilty of turning under residues high in carbon and low in phosphorus content. Such materials not only would supply little phosphorus directly but might appreciably reduce the supply of available soil phosphorus for an indefinite period. This has been demonstrated, for example, by Papadakis (1947), who concluded that the adverse effect of added straw on plant growth was due to the immobilization of inorganic soil phosphorus by microbial action. One of the difficulties encountered is that of predicting how long a period of time must elapse before net immobilization gives way to net mineralization of phosphorus. As discussed in Chapter V, a knowledge of the carbon:phosphorus ratio does not provide a wholly satisfactory basis for such a prediction. Proper control of factors such as supply of available nitrogen and other nutrients, pH of the soil, and aeration should favor earlier release of the phosphorus by increasing the rate of decomposition.

Some interesting results relating to these factors have been obtained through the use of plant materials tagged with radiophosphorus. Fuller and Dean (1949), using heavy applications (20 to 30 tons per acre) of acid-extracted soybeans and wheat tops, containing 0.15 and 0.11 per cent phosphorus, respectively, noted very marked reductions not only in yield but also in phosphorus uptake by the rye grass. Interpretation of the results is complicated by the fact that acid extraction not only removed the inorganic phosphorus but also widened the carbon:phosphorus ratio of the plant material. With advancing stage of maturity of barley hay added to calcareous soils, Fuller and Rogers (1951) observed a reduction in phosphorus uptake by rye grass. This effect might be attributed, in part, to a widening of the carbon:phosphorus ratio and to changes in the nature of the carbon constituents.

From the preceding discussion it is evident that further comprehensive investigations employing radiophosphorus are needed to evaluate phosphorus availability in green manures in relation to soil and environmental factors which influence decomposition of organic materials and phosphorus availability.

b. Farmyard Manure. In the moist state farmyard manure may be expected to contain about 4 to 6 pounds of P_2O_5 per ton, the actual figure being dependent upon the source, the proportion and kind of litter used, the stage of decomposition, and the extent to which loss of water-soluble forms of phosphorus has occurred. Salter and Schollenberger (1939) concluded that the availability to plants of phosphorus in farmyard manure is equal to, or in some instances exceeds, that applied in chemical fertilizers, although Stewart (Chapter XIV) considers that chemical sources are superior. The occasionally observed superiority of the manure phosphorus over chemical forms has been attributed to various indirect effects (Salter and Schollenberger, 1939; Dalton *et al.*, 1952).

Studies at Cornell University in which manure tagged with radiophosphorus was employed have shown a relatively high availability of manure phosphorus to plants. McAuliffe *et al.* (1949) reported the first experiment of this kind in 1949. Utilization of phosphorus in sheep feces, labeled with P^{32}, was compared with that utilized by Italian rye grass from tagged superphosphate. It was found that the availability of phosphorus from these two sources was nearly the same. Similar results were obtained more recently by McAuliffe and Bradfield (1952) in a study conducted in outdoor concrete frames. At the end of 27 days, Sudan grass had derived essentially the same percentage of its phosphorus from cattle manure as from superphosphate. With the next two cuttings taken at 48 and 69 days after planting, the availability of the

phosphorus from manure exceeded that from superphosphate on all soils, the basis for comparison being the percentage of phosphorus in the plant derived from these two sources. This may be explained in part, however, by the fact that the manure supplied somewhat higher amounts of phosphorus (approximately 150 compared to 115 pounds P_2O_5 per acre from superphosphate). As in the earlier study, the manure contained a rather high proportion of inorganic phosphorus (77.4 per cent), and there was no litter mixed with the manure.

According to these investigations, therefore, reduction in availability of phosphorus in manure due to immobilization is not likely to be of much consequence where decomposable litter has not been included. However, immobilization may be a factor in cases where straw or other such litter is used in large quantity, as pointed out by Kaila (1949) and indicated in the previous discussion of green manures and crop residues.

2. *Indirect Effects on Phosphorus Availability*

a. Native Soil Phosphorus. Various statements may be found in the literature to the effect that the turning under of green manures or farmyard manures increases the availability of *soil* phosphorus to plants. It is not often, however, that such conclusions are substantiated by experimental data.

Various investigators have attempted to deduce the cumulative effects of green manures, crop residues, or farmyard manures applied to field plots upon the availability of *soil* phosphorus (Kubota *et al.*, 1947; Reynolds and Smith, 1946; Moser, 1942; Royer *et al.*, 1948; Copeland and Merkle, 1942). The results have been inconclusive in most instances because of inherent weaknesses in the experimental designs; in certain instances, the solubility of phosphorus in various chemical extractants constituted the chief criterion for assessing changes in the soil phosphorus status. It is recognized that certain difficulties are encountered in designing suitable experiments for distinguishing between the effects of organic matter as such and its indirect effects on the availability of soil phosphorus. Factorial experiments in which it is possible to determine the interaction of manure and phosphorus effects under different soil conditions hold some promise. Results from three such experiments being conducted in Iowa thus far indicate that an application of 6 tons of manure every 3 years in a rotation of corn, oats, and meadow has been more effective than an approximately equivalent amount of phosphorus supplied as ordinary superphosphate, both as reflected in yields and phosphorus uptake by corn.

It has long been recognized that carbon dioxide production in soils may bring about increased availability of the soil phosphorus. McGeorge (1939) and McGeorge and Greene (1935) considered that the beneficial effect of applying organic materials to calcareous soils could be explained to a considerable extent by the action of the carbon dioxide liberated and the accompanying reduction in pH value of the soil. Stephenson (1938) also concluded that carbonic acid is of considerable significance in neutral or calcareous soils; but that it exerts little solvent action on soil minerals in acid soils. Recent evidence presented by Gerretsen (1948), however, suggests that the action of carbon dioxide in solubilizing phosphate compounds may extend over a rather wide range of soil conditions. The evidence, therefore, is rather convincing that carbon dioxide production in well-aerated soils exerts a favorable influence on phosphorus availability.

Of equal or possibly even greater significance is the evidence that other compounds resulting from organic matter decomposition may also be active in making soil phosphorus more available. Jensen (1917) concluded that water extracts of decomposing plant materials were much more effective than water in dissolving phosphorus from soils. Since then humus extracts from soils or composts have been reported by a number of investigators to increase the solubility of phosphorus in soils (Boischot and Sylvester, 1949; McGeorge and Greene, 1935; Chaminade and Vistelle, 1947; Swenson *et al.*, 1949) or to increase its availability to plants (Chaminade and Blanchet, 1952); and a number of mechanisms have been proposed to explain the action of so-called humic substances on phosphorus solubility. Chaminade (1943) and Chaminade and Blanchet (1952) have ascribed the beneficial action to formation of phosphohumic complexes; the phosphorus in these complexes is regarded as being more assimilable by plants than that of difficultly soluble soil phosphorus compounds. Anion replacement or competition between humate and phosphate ions for seats on adsorbing surfaces also has been proposed to explain the benefits derived (Boischot and Sylvester, 1949; Barbier *et al.*, 1951). Gaarder and Grahl-Nielsen (1935) found lower amounts of water-soluble phosphorus in soils poorly supplied than in soils well supplied with organic matter; this difference was evident over a wide pH range. They suggested that humus colloids form protective coatings over the colloidal sesquioxides, thus reducing the phosphate-fixing capacity of the soils.

Attempts at explaining the role of humus preparations in rendering soil phosphorus available to plants have always been hampered by insufficient knowledge concerning the chemical constituents responsible for the action and the nature of the specific reactions which might be

involved. In recent investigations at the Massachusetts Experiment Station by Sieling and his associates, however, considerable evidence has been obtained supporting the view that the addition and decomposition of plant residues or manures provide certain organic anions which react with iron and aluminum to form complexes (Swenson *et al.*, 1949; Struthers and Sieling, 1950; Dalton *et al.*, 1952). Moreover, they consider that such reactions may commonly occur in soils and not only reduce fixation of added phosphate ions, but also bring about dissolution of native iron and aluminum phosphates. In a systematic investigation of the replacing ability of various organic anions, Struthers and Sieling (1950) observed that those anions which were most effective in replacing phosphate—citrate, oxalate, tartrate, malate, and malonate—are also the ones which are probably produced in abundance during decomposition of organic matter by microorganisms.

Evidence has also been obtained that pectic acid and galacturonic acid act as very effective complexing agents *in vitro* (Sieling and Struthers, 1950; Bradley and Sieling, 1953). The possible significance of this finding is at once evident, since pectin is found in all plant tissues, and galacturonic acid is one of the products resulting from hydrolysis of pectin. Further, these workers call attention to the occurrence of uronides in soils in considerable amounts and the possible importance of these substances in mobilizing phosphorus.

A few studies have been conducted in order to determine whether or not the beneficial action of organic matter additions upon solubility of soil phosphorus, as indicated above, is reflected in increased phosphorus uptake by plants. This is not easily demonstrated where organic materials contain phosphorus, except possibly through the use of materials tagged with radiophosphorus. Recognizing this difficulty, Dalton *et al.* (1952) in some recent work used phosphorus-free starch and glucose and found that the total phosphorus uptake from an acid sandy loam soil by six cuttings of Ladino clover and one crop of corn was practically the same as that recovered from a 160-pound P_2O_5 application as KH_2PO_4. Pectin alone had little influence on phosphorus uptake from the soil, although laboratory studies showed pectic acid to be an effective complexing agent with iron and aluminum (Sieling and Struthers, 1950). Since all three materials, however, exerted pronounced effects on the availability of phosphorus in rock phosphate, it seems possible that the beneficial effects were due to increased CO_2 production.

Certain studies, using plant residues tagged with radiophosphorus, also show that utilization of soil phosphorus was increased by incorporation of green manures (Fuller and Dean, 1949; Nielsen, 1952); others have shown no such effect (Fuller and Rogers, 1951; McAuliffe *et al.*,

1949, 1952). The results of Nielsen (1952) are of particular interest. He found that ground alfalfa placed in Wooster silt loam soil enabled the corn plants to obtain considerably more soil phosphorus than when an equivalent amount of phosphorus was applied as KH_2PO_4. He points out that the dissolution of iron and aluminum phosphates by organic acids produced during decomposition may have accounted for the increase; he suggests also that the solubility of calcium and magnesium phosphates might have been increased in areas of high carbon dioxide evolution from the decomposing alfalfa. The soils were taken from plots which ranged in pH from 6.3 to 6.8; thus, the presence of calcium and magnesium phosphates is indicated. Further investigation is needed to clarify the release mechanisms involved.

It is well established that increases in phosphorus availability often are associated with liming (see Chapter IX). It is also well known that liming stimulates microbiological activity. Struthers and Sieling (1950) have suggested that the increases in phosphorus availability associated with liming of acid soils may be due primarily to the presence of greater quantities of organic anions produced as a result of stimulated microbiological activity. This might explain in part the fact that in some soils liming does not greatly increase phosphorus availability (Struthers and Sieling, 1950; Aslander, 1950). Aslander (1950), in Sweden, takes the interesting view that liberal application of phosphorus with manure may eliminate the need for liming, even under very acid soil conditions. Evidently there is a need for carefully investigating, under different soil conditions, the interaction of lime effects with organic anion effects in order to determine whether or not these factors operate independently in raising the level of available phosphorus supplied to plants.

On the basis of the available evidence, it is clear that the addition of organic materials to soil may increase the availability of native soil phosphorus. Of particular interest is the hypothesis that organic anions capable of hastening the solution of iron and aluminum phosphates are present in soils. It has not been demonstrated, however, that organic acids are produced or persist in sufficient abundance to account for appreciable effects on phosphorus solubility in soils.

b. Fixation of Applied Phosphorus. Certain of the mechanisms which have been proposed to account for the beneficial effects of organic matter on solubility of native soil phosphorus also may explain the reduction in fixation of applied phosphorus which often occurs when organic matter is added to soil.

Various investigators have clearly demonstrated that organic matter additions reduce the capacity of soils to fix added phosphorus as determined by recovery of phosphorus by various extracting reagents

(Rhoades, 1939; Barbier *et al.*, 1951; Yuen and Pollard, 1951; Walsh *et al.*, 1950). Almost twenty years ago, Steele (1934) in studying the influence of various organic anions on phosphorus fixation by various soil colloids found that citric, oxalic, and humic acids were effective in reducing fixation of added phosphates. The more recent investigations of Swenson *et al.* (1949), Struthers and Sieling (1950), and Dalton *et al.* (1952) likewise show that various organic anions, several of which they believe occur in soils, are very effective in reducing fixation of phosphorus in the presence of iron and aluminum. If, therefore, it can be shown that these organic acids occur in soils in appreciable amounts, it would provide strong evidence that the beneficial effect of organic matter may be explained in part by its effect in increasing the availability of native or applied phosphates.

The work of Midgley and Dunklee (1945) has been particularly valuable in showing that superphosphate is much more effective when intimately mixed with manure prior to application than when these materials are applied separately. In one experiment on an acid B horizon of a podsol, the yield of tomatoes was three times greater with mixing than with separate application. A comparison of these two methods of applying 20 per cent superphosphate (500 pounds per acre) and manure (10 tons per acre) on a wide range of soils under greenhouse conditions showed that the advantage of intimate mixing was greatest on soils possessing rather high phosphorus-fixing capacities. Confirming results were obtained in a number of field experiments. These workers consider that the beneficial effects of mixing superphosphate and manure result from a reduction in exposure of the phosphate to fixing agents in the soil. Similarly, Hester and Shelton (1937) demonstrated some striking increases in the effective use of superphosphate by plants from adding various organic materials to a Norfolk fine sandy loam containing a low content of organic matter. From a practical standpoint, therefore, the relationship of phosphorus fixation to organic matter appears to be important, although the mechanisms involved are not yet clear.

III. Rate, Time, and Frequency of Application

The efficient use of phosphorus fertilizers depends not only on soil deficiency and crop requirements but also on the factors of rate, time, and frequency of application, as well as the method of application. These latter factors all influence phosphorus availability in soils largely by affecting the degree and rate of fixation of the applied phosphorus. Because they are closely related in practice, it is often difficult to evaluate their separate effects. Moreover, any one of these factors may

greatly affect the importance of another. For example, the importance of time may be greatly influenced by the rate or method of application, and vice versa.

1. Rates of Application and Residual Values

Ideally, phosphate fertilizers should be applied at rates which result in maximum financial return. This optimum level of fertilization is reached when the value of the increase in crops resulting from a small additional increment of fertilizer is equal to the costs involved in producing the extra increment of yield (Crowther and Yates, 1941). This concept assumes that capital is not a limiting factor. It should not be confused with the more generally accepted view that most efficient use is attained when the rate of application is such that the ratio of value of crop increases to fertilizer costs, taking other costs into account, is near the maximum. In either of these approaches, the rate of phosphate application is determined by the responsiveness of the soil to phosphate, the cost of fertilizer, the value of the crop, and additional costs (planting, harvesting, and marketing, for example).

According to another view, less widely accepted, it is held that the phosphorus status of the soil should at once be built up to some desired level, which may be considerably beyond that required for maximum yields. An attempt is then made to maintain this level by periodic applications of phosphorus (Truog *et al.*, 1945). This concept has been variously justified on the basis that a heavy initial fertilizer application essentially constitutes a capital investment; and that residual effects from heavy application may be relied upon to supply the phosphorus needs in case of short fertilizer supply or adverse economic conditions.

The writers do not propose to present arguments for or against the general concepts regarding rate of application here outlined, or the various modifications of these which might be considered. Such a discussion revolves around economic as well as agronomic principles. The first requirement, of course, is to establish a firm foundation, based on suitable experimental evidence, for evaluating any and all systems of fertilizer use. Some of the questions which need to be answered more fully are: What is the relation between response and rate of phosphorus application for different crops grown on different soils? How are responses related to time and frequency of application, placement of fertilizer, drainage, irrigation practices, and various other soil and crop management practices? What are the magnitude and duration of residual effects obtained from various rates of phosphorus fertilizer application, and how do these affect response to subsequent phosphorus applications? These are some of the more important questions that must

be answered as the agronomist joins with the economist in working out realistic systems of efficient phosphorus use based on quantitative data.

There is ample evidence that many farmers are applying phosphorus fertilizers at rates which are considerably lower than those needed to give maximum returns, under existing economic conditions. The ratio of farm prices to fertilizer prices is extremely favorable, and this situation is apt to continue. In view of this situation, it is to be expected that many farmers will continue to increase the rates of phosphorus fertilizer applications in the direction of securing maximum financial returns.

Application of phosphorus fertilizer in amounts greater than are utilized by the crops must inevitably result in an accumulation of total and available phosphorus in the soil if soil erosion is controlled. The value of these accumulations in terms of residual effects on crop yield has not been thoroughly investigated for a wide range of conditions. At present, in this country, the residual value of previous phosphorus applications is largely ignored in landlord-tenant relationships, principally because there is little sound basis for evaluating it in terms of magnitude and duration of expected crop yield increases. This constitutes a serious obstacle to the adequate and efficient use of fertilizers on the many tenant-operated farms in this country.

The magnitude of the residual effect may be extremely low in certain instances, even with large applications of phosphorus. As an extreme example, McAuliffe *et al.* (1951) reported that applications of 1000 and 2000 pounds per acre of 20 per cent superphosphate to two silt loam soils in New York in 1941 showed very small residual effects in 1949, as reflected in growth and phosphorus uptake from the soil by oats and by soil tests for available phosphorus. Williams (1950) also noted large losses in the effectiveness of superphosphate applied to acid soils. In other instances, however, residual or cumulative effects from past applications of phosphorus have been found to be appreciable. (Rich *et al.*, 1947; Pierre, 1938; Bushnell, 1950; Volk, 1945; Peech, 1945; Robinson and Pierre, 1938; Weeks and Miller, 1948.) Scattered evidence obtained on certain western and midwestern calcareous soils indicates that residual effects from superphosphate applications also may be rather large (McGeorge and Breazeale, 1936; Converse, 1948; Stanberry, 1948; Lyons *et al.*, 1944; Larson *et al.*, 1952). Relatively high residual effects from superphosphate, applied at a rate as low as 60 pounds P_2O_5 per acre, are evident in the data of Table I. On the calcareous soils of Alabama, however, Scarseth (1932) found low residual effects even from rather large applications. (See also Chapter XIII.)

In general, it is to be expected that residual effects will be relatively

TABLE I

EFFECT OF VARYING THE FREQUENCY AND RATE OF APPLYING TREBLE SUPERPHOSPHATE ON CROP YIELDS IN A ROTATION OF CORN, OATS, AND TWO YEARS OF ALFALFA-BROME GRASS MEADOW[a]
(Ida silt loam, pH 7.8)

Treatment			Yields				
				Meadow, tons/acre			
Treatment	P_2O_5 applied, pounds/acre	Crop fertilized	Oats, bushels/acre	1st-year	2nd-year	Total	Corn, bushels/acre
1	None	.....	22.8	0.70	0.92	1.62	15.3
2	60	Oats	41.9	1.96	1.78	3.74	26.2
3	120	Oats	46.6	3.24	2.72	5.96	36.5
4	240	Oats	47.1	3.18	3.75	6.93	62.4
5	60	Oats					
	60	2nd-year meadow	39.6	2.44	3.60	6.04	45.4
6	60	Oats					
	60	Corn	38.2	2.88	2.61	5.49	55.6

[a] Two-year average yields are given for oats and corn; only 1951 yields of meadow are given, since complete data are not available for 1950, as a result of winter-killing.

low on acid soils and will be increased by liming, although the relationship will vary depending on the nature of the soil. It is evident, however, that there is a need of more basic data on the residual effects of phosphorus fertilizers applied at different rates. The method for evaluating availability of soil phosphorus recently proposed by Fried and Dean (1952) appears to hold some promise as a means of studying both the magnitude and duration of residual effects from previous phosphorus applications.

2. *Time of Application*

Increasing interest is being expressed by agronomists, those in the fertilizer industry, and farmers alike in the feasibility of applying phosphorus fertilizers within the period of several months prior to planting the crop. There are various reasons for this interest, most of which are based on economic considerations. It would be economically advantageous to the manufacturer and to those engaged in bulk spreading of fertilizers, for example, to extend the period of fertilizer application. Greater flexibility with respect to time of application oftentimes would enable the farmer to use his supply of labor more efficiently. Fall applications, for example, would lessen the work load at the critical period of planting the crop in the spring. These few considerations serve to point up the practical importance of considering time of fertilizer

application. The present discussion will be concerned primarily with two aspects of this problem namely: (1) application at time of planting versus application several weeks or months in advance of planting the crop, and (2) applications to established meadows or pastures.

The limited amount of work on this problem indicates considerable variations in the reduction of availability of phosphorus fertilizer applied several months prior to planting the crop. Thus, Scarseth (1932) found that applying 250 pounds per acre of superphosphate at the time of planting soybeans on some Alabama clay soils produced as much growth as 1000 pounds applied 6 months before planting. In a greenhouse study of six Iowa soils ranging in pH from 5.1 to 7.6, Bower (1945) found that the response of oats to a 200-pound per acre application of superphosphate was 23 to 46 per cent less when mixed with the soil 3 months before planting than when applied at planting time. Even greater reductions were obtained by Thorne (1941), using the tomato plant as the test crop. On the other hand, several workers concluded from their studies on some western calcareous soils (Lewis *et al.*, 1950; Wursten, 1948) that a difference of several months in time of application was of little importance.

There are a number of factors which influence the relation between time of application and effectiveness of applied phosphorus fertilizer, but the most important is undoubtedly the fixation capacity of the soil. On acid soils, liming is of primary importance in reducing phosphorus fixation (Chapter IX). Another important consideration is the rate of application. Thus, if the rate of application is in excess of that required for maximum efficient use by the crop in question, there may be no apparent or measurable difference in effectiveness, whether the phosphorus is applied in the fall or at time of planting in the spring. In such a case, measurements of residual effects on succeeding crops are necessary in evaluating the practices. There is also the effect of placement of the phosphorus fertilizer on the loss of effectiveness during the first few months after applications are made. Thus, band placement can be expected to result in a greater residual effect than mixing the phosphorus with the soil. Another important consideration is that any advantages associated with specific placement of phosphorus fertilizer with respect to the seed at time of planting on certain crops is largely lost as a result of early applications, as discussed in Section IV.2.a. From the practical standpoint, therefore, the gains in economy and convenience that result from early application need to overbalance any losses in effectiveness of the phosphate if the objective is to secure maximum profitability of the phosphorus applied.

The problem of when to apply phosphorus fertilizer to established

pastures or meadows involves considerations which are not encountered in fertilizing annual crops. On established stands, the phosphorus usually is top-dressed or drilled. In the latter case, contact between soil and fertilizer is reduced to a minimum, which should also minimize phosphorus fixation. Moreover, recent work shows that during the period of active growth the phosphorus from broadcast applications is quickly and effectively utilized by the crop under favorable soil moisture conditions (see also Section IV.2.b). Cook (1951) found no differences in response of alfalfa to a top-dressing of 300 pounds of 0-16-0 per acre, whether the fertilizer was applied in July or in October of the preceding year, or in April of the year in which yields were measured. Similar results were obtained by Lyons *et al.* (1944) in drilling superphosphate on alfalfa stands.

3. *Frequency of Application*

The problem of frequency of application in the rotations or to permanent pastures is of importance throughout the range of phosphorus-deficiency levels encountered in soils. Even with soils in the range of slight deficiency, there is the question of properly placing small quantities of phosphorus on certain crops to achieve so-called "starter" effects, i.e., early growth stimulation; examples are the use of starter fertilizer solutions with tomatoes and light hill or row application for corn. As the need for phosphate fertilization becomes more pronounced, the importance of frequency of application in relation to phosphorus effectiveness becomes progressively greater. Also, it is evident that frequent applications are likely to be more important with soils of high fixing capacities.

Very few comprehensive experiments have been reported in which comparisons have been made between splitting the application of a given quantity of phosphorus among all crops in the rotation versus applying all at once or to particular crops in the rotation. Results of an experiment being conducted in Iowa on a calcareous Ida silt loam soil will serve to illustrate the practical nature of the problem in a situation of extreme deficiency. In this study, a 4-year rotation of corn, oats, and 2 years of meadow (alfalfa-brome grass) is being followed. The effect of a single application to oats (120 pounds P_2O_5 per acre), as compared to that of split applications to various crops in the rotation, is shown in Table I. Splitting the 120-pound P_2O_5 application between oats and second-year meadow, compared to applying it all to oats, reduced oat yields by 7 bushels but increased the yield of corn 9 bushels per acre. Splitting the phosphorus between oats and corn, compared to applying it all to oats, decreased oat yields by 8 bushels, and hay yields by ½ ton

in 2 years, but it increased the yield of corn 19 bushels per acre. It is obvious, therefore, that splitting the application was desirable on this calcareous soil. Whether or not this would hold if the rate of application were doubled is not evident from the experiment.

As larger amounts of phosphorus fertilizer are applied in the rotation, a point must finally be reached where a single application will suffice to give maximum or near-maximum effects on all crops. This point will, of course, be affected by the fixing capacity of the soil. That such an application may be very great in certain instances is strikingly demonstrated by some experiments reported by Williams (1950). One year after applying 2500 pounds of 20 per cent superphosphate to some acid soils, he found that additional phosphorus was needed for maximum yields of swedes or turnips. Basing his conclusion on evidence of this kind, Williams (1951) concluded that a suitable application should be given to each crop rather than heavier applications infrequently in the rotation, especially on soils which possess high phosphorus-fixing capacities. This is, in general, the conclusion of most American workers. Frequent application in the rotation also makes it possible to obtain the advantage from specific placement of phosphorus fertilizer to individual crops, as indicated in Section IV.2.a. (See also Chapter XIII.)

Frequency of application may also be an important consideration in efficient use of phosphorus on permanent pastures. On the basis of an opinion survey conducted in 1950, Dodd (1951) reported that a high proportion of the agronomists in the Northcentral and Eastern States considered annual or biennial applications of phosphorus on pastures to be more efficient than applications every 4 years. Robinson and Garber (1949), however, point out, on the basis of available evidence, that heavy infrequent application may be superior to lighter, more frequent applications on very phosphorus-deficient soils.

It seems evident that the initial application, at least, should be large enough to raise the available phosphorus content of the soil to a point necessary for good growth, or to bring about the desirable changes in plant species.

IV. Placement or Method of Application

1. Crops in the Rotation

Even under optimum condition of soil reaction, soil structure, drainage, moisture, and other factors, which directly or indirectly exert influences on the phosphorus nutrition of plants, crops generally are unable to recover more than a relatively small proportion of the phosphate applied in fertilizers. This is in marked contrast to the situation with

nitrogen or potassium fertilizers, where recovery often is higher than 50 per cent. Both fixation of phosphorus and positional unavailability have been regarded as the factors primarily accounting for low recovery of applied phosphorus by crops. Thus, the increased benefits obtained from band application as compared to broadcast applications of phosphorus fertilizers in many instances have been attributed to reduced fixation resulting from less intimate contact between soil and fertilizer, greater accessibility of the applied phosphorus to plant roots, or a combination of these and other factors.

Early investigations by Coe (1926) with oats and clover seedings and by Duley (1930) on wheat clearly demonstrated that drilling phosphorus in contact with the seed was much superior to broadcasting. These early experiments have been amply confirmed in numerous studies conducted since that time. Various references are found to the effect that when drilled, only about half as much phosphorus fertilizer may be required to produce a given yield increase as when the fertilizer is broadcast (Reith, 1952; Smith, 1947; Lewis and Strickland, 1944; Norum and Young, 1950). Evidence of the widespread interest in fertilizer placement on many crops during the past decade or longer is contained in the various Proceedings of the National Joint Committee on Fertilizer Application.

Recently, further impetus has been given to research on placement methods as a result of developments in the use of radiophosphorus in field investigations. Until tagged phosphate fertilizers came into use, it was not possible to evaluate clearly the relative or actual amounts of phosphorus obtained by the plant from various placements. This new development in research has greatly stimulated investigations along two main lines: (1) comparisons of different types of placement for various crops, and (2) evaluation of the factors or variables which may determine the relative value of different placements.

In general agreement with earlier evidence, the studies with radiophosphorus conducted during recent years have demonstrated that crops generally derive greater amounts of phosphorus from localized placements, such as banding or mixing with a restricted volume of soil, than from broadcast applications (Nelson *et al.*, 1949; Blaser and McAuliffe, 1949; Caldwell *et al.*, 1950; Pesek, 1951, Welch *et al.*, 1949; Speer *et al.*, 1951). As discussed in Chapter VII, however, there are marked differences in the behavior of different phosphorus fertilizers in relation to placement.

Among the many factors which may determine the superiority of a particular system of placement over another, the kind of crop and its pattern of root distribution appear to be of particular importance, as

indicated in recent studies reported by Hall (1951). Using a technique involving injection of small quantities of radiophosphorus at various positions in the soil with respect to the plant, he found, for example, that corn relies heavily on the top 3-inch layer of the soil during the first few weeks of growth but not after this time. By the end of 7 weeks, the 8-inch and 13-inch horizons contribute substantially to the growth of the plant.

The foregoing observations may help to explain results of previous studies which have shown relatively high uptake of fertilizer phosphorus by the corn plant early in the season, but a rapid decline after 4 or 5 weeks (Nelson *et al.*, 1949; Stanford and Nelson, 1949; Rich *et al.*, 1949; Jackson *et al.*, 1950). Viewed as a whole, the studies with root distribution and utilization of fertilizer phosphorus suggest the need for further investigations to determine the value of placing phosphorus in bands at various depths compared to placing it at one depth, as a means of more effectively supplying phosphorus to the crop during critical periods of growth, and as its root system develops in the deeper horizons of the soil. In this connection, Drake and Stewart (1950) recently found a significant positive interaction between 3-inch and 8-inch depth drill placement for alfalfa; this illustrates a possible advantage from multiple band placement which is worthy of special study.

Moisture conditions in the soil greatly influence the ability of plants to obtain phosphorus from fertilizer placed at different depths in the soil. In agreement with results obtained by Scarseth (1943), unpublished data from a large number of corn fertilizer experiments in Iowa during the past several years have shown that fertilizer phosphorus which is shallow-placed along the hill or row is often poorly utilized in dry seasons, whereas that placed at plow-depth may be very effective. On the other hand, under favorable moisture conditions, such as prevailed in most of Iowa during 1950 and 1951, both placements were very effective and negative interactions occurred between plowed-under and row-placed fertilizer. Haddock (1952) recently found that placement had little influence on uptake of fertilizer phosphorus by sugar beets when the soil was well irrigated. However, with less irrigation the placement 4 inches deep in bands was more effective than surface broadcast placement. Olsen *et al.* (1950), also noted little difference between placements under favorable moisture conditions but considerable advantage to deep band placement in a relatively dry season.

One of the advantages commonly attributed to band placement of phosphorus fertilizer beside the hill or row, or drilling with the seed as is often the case with small grains, is the early growth stimulation which it promotes. This often produces a variety of effects which may

be attributable at least indirectly to phosphorus. Thus, in adverse seasons the more rapidly growing plants may better resist the inroads of insects and disease, resulting in increased stand; greater tillering of small grains sometimes occurs with band than with broadcast placement, as was early demonstrated by Duley (1930) in comparing drilled versus broadcast application for wheat. Norum and Young (1950) have also emphasized that the ability of wheat to compete with weeds was relatively greater with band than broadcast application. From a practical standpoint, however, these may be regarded as being effects of the fertilizer, whether direct or indirect, and serve to emphasize a well-known fact that benefits obtained from fertilization are very much dependent upon other factors. An understanding of the interactions of placement with other factors is, of course, fundamental to sound fertilizer use.

2. *Permanent Pastures and Long-Time Meadows*

a. At Time of Stand Establishment. The problems of placement of fertilizers in the establishment of long-time meadows and pastures and in the renovation of the latter through soil preparation and reseeding are similar. In most cases the objective is (1) to incorporate the phosphorus in the soil at time of seed-bed preparation, and (2) to apply enough phosphorus to assure good seedling establishment as well as high yields of forage for a period of several years (Robinson and Garber, 1949). As with small grain seedings previously discussed, it is generally recognized that band applications are more effective than incorporation by broadcasting on the surface, followed by discing. Recent work with radiophosphorus has in general supported this conclusion. Thus, Blaser and McAuliffe (1949) found that Ladino clover on Mardin silt loam in New York derived a significantly higher percentage of phosphorus from drilled than from broadcast applications during the first few months of growth, although this was not the case with orchard grass. Likewise, Hervey *et al.* (1950), in establishing sweet clover on a calcareous Blackland soil of Texas, found that drilling the phosphorus 2 inches deep resulted in a much greater percentage of phosphorus being absorbed from the fertilizer tagged with P^{32} than did broadcasting. Moreover, the yield was higher and the amount of phosphorus found in the roots to a depth of 18 inches was 77 per cent greater.

Recently, the importance of more specific placement of phosphate with respect to the location of the legume and grass seed has been emphasized by Haynes and Thatcher (1950) in Ohio. Placing the fertilizer about 1½ inches directly below the seed gave seedling performance

superior to that given by any other method studied. When the seed was placed as little as ½ inch to one side of the fertilizer band, much poorer seedling growth resulted.

Deep placement of phosphate at time of stand establishment, in addition to shallower drill placement, may also be desirable, as is indicated by the work of Drake and Stewart (1950). Working with Cecil clay loam soil in South Carolina, they found that the banding of superphosphate 8 inches deep was much more effective than banding 3 inches deep when used in addition to the basic application, the increase in yield for the 2-year period being 2070 pounds and 790 pounds, respectively. During dry weather, plants were observed to wilt less with phosphorus banded at 8 than at 3 inches deep, emphasizing the importance of deep placement on root distribution. This study suggests the possibility of two placements of phosphorus fertilizer at the time of establishing meadows and pastures, one near the seed to help get seedlings established quickly, and a deeper placement in the subsurface soil as a means of increasing the availability of moisture and phosphorus to the plants.

b. Applications to Established Stands. Top-dressing has long been the means employed for applying phosphorus and other nutrients for established meadows and permanent pastures. Research workers, however, have not been entirely satisfied with the method. On old permanent pastures containing a predominance of undesirable grasses and little or no legumes, it often takes several years before much improvement in yields is obtained (Robinson and Pierre, 1938). This is partly due to the time required for the more productive species to become established, but also probably to the slow downward movement of the phosphorus.

There is ample evidence that the downward movement of phosphorus applied as a top-dressing is very slow. Sell and Olson (1947) recently reviewed this subject. In their own investigations they found no detectable movement below 1 inch in a sandy loam soil during a period of 3 years when 80 pounds P_2O_5 as superphosphate was applied as a top-dressing. With heavier soils, silt loams and clay loams, the movement is even slower. Schaller (1941), for example, found no downward movement of phosphorus below 1½ inches where a total of 1000 pounds of 0-20-0 had been applied 5 to 7 years previously on a deKalb silt loam and on an Upshur silty clay loam soil in West Virginia. Likewise Brown (1935) found no downward movement below 2½ inches on permanent pasture plots which had been fertilized for 16 years with superphosphate at the rate of 65 pounds P_2O_5 every 2 years.

In spite of the theoretical shortcomings of top-dressing of phos-

phorus fertilizers, the more recent results of field experiments with meadows and pastures have given increased support for this practice. Some striking responses from phosphorus top-dressing, for example, were obtained in 1944 in northern Iowa on established alfalfa fields on very phosphorus-deficient soils (Nelson *et al.*, 1946). Three hundred pounds of 20 per cent superphosphate applied as a top-dressing in the spring of 1944 increased the yields that year from 0.48 to 1.0 ton per acre per cutting. In the following year the untreated plots yielded 0.42 ton and the plots that had received top-dressing yielded 1.35 ton per cutting. Moreover, the percentage of phosphorus in the alfalfa hay in 1944 was increased from 0.13 per cent to 0.19 per cent, or an increase of over 40 per cent. More recently, similar results have been obtained on a wide range of soils (Stanford and Hanway, 1951; Lawton *et al.*, 1947).

Even more convincing are recent data obtained with radioactive phosphorus fertilizers, showing definitely that established meadows and pastures may readily absorb phosphorus applied as a top-dressing (Table II) (Stanford *et al.*, 1950). Likewise, rapid absorption of the

TABLE II

PERCENTAGE OF PHOSPHORUS IN THE PLANT WHICH WAS DERIVED FROM SURFACE-APPLIED SUPERPHOSPHATE AT TWO RATES OF APPLICATION[a,b]

Superphosphate application, pounds/acre	*Alfalfa*[c]		*Ladino clover*		
	1st cut	*2nd cut*	*Orchard*[c] *grass*	*Caldwell field*[c]	*Mt. Pleasant field*[d]
200	20.0	19.5	15.8	23.8	17.8
1000	45.9	47.0	43.9	60.0	49.5

[a] Stanford *et al.* (1950).

[b] Superphosphate broadcast on April 20. The samples of Ladino clover, orchard grass, and first cutting of alfalfa were taken on June 15; the second cutting alfalfa samples were taken on August 5.

[c] Dunkirk silt loam at Caldwell field.

[d] Mardin silt loam.

phosphorus applied as top-dressings to alfalfa stands was obtained under adequate moisture conditions by Caldwell *et al.* (1951), in Minnesota, and by Pesek (1951) in Iowa. It is apparent, therefore, that the roots within the surface ½ inch or so of soil must be very active in absorption, for in these experiments most of the phosphorus is undoubtedly retained in the surface ½ inch or less of the soil during the first few months after application. Dodd (1951) has emphasized recently that grasses, and legumes to a lesser degree, develop roots on or very near the soil surface during periods of moist soil conditions. Moreover, from

the standpoint of fixation, top-dressing applications come in contact with less soil than applications thoroughly disced into the upper 2 or 3 inches. Loss in availability may, therefore, be less, especially in permanent pastures where the surface layer is high in decomposing plant residues.

From the standpoint of both positional and chemical availability of the applied phosphorus, however, it would be expected that band placement of the fertilizer 1 inch or more below the surface of the soil would be preferable to top-dressing. The use of a combination grain-fertilizer drill has been advocated for this purpose and has proved effective on established meadows (Lyons *et al.*, 1944). Midgley called attention to the effectiveness of subsurface-band placement of phosphorus on permanent pastures in 1931, but relatively little work has been done on this problem since. In 1938 several workers (Dodd, 1938; Mulvey *et al.*, 1938; Cook, 1938) reported on some placement studies with phosphorus on permanent pastures. Their studies, which included band placement of the fertilizer to depths of 2 to 3½ inches, did not indicate any superiority for this practice over top-dressing, but they represented only 1 to 2 years of work. More recently there has been some renewal of interest in this problem, especially in the Southeastern States, where the Tennessee Valley Authority in cooperation with several of the agricultural experiment stations, has been investigating the use of experimental machines for subsurface placement of fertilizer to sod crops (Hines, 1951). Preliminary results reported from the Kentucky and Virginia Agricultural Experiment Stations comparing top-dressing and subsurface applications to a depth varying from 2 to 6 inches, are largely negative (Fergus and Thaxton, 1952; Rich *et al.*, 1952). In fact, there is evidence in some of the experiments that top-dressing gave better results during the first year of the experiment than subsurface drilling (Fergus and Thaxton, 1952). This agrees with some recent results obtained by Haley (1951) in Indiana. Haley obtained significantly greater yields during the first 2 years after application from broadcasting on the surface than from band placement 6 inches deep and 12 inches apart. These studies, however, have not been continued long enough or under sufficiently different conditions to adequately test the value of subsurface applications. Rich *et al.* (1952) also compared broadcast applications of phosphorus with applications in bands 6 inches apart on the surface and 2 inches deep on established meadows and pastures. No responses in yield were obtained, but much higher absorption resulted during the first year from broadcast applications than from the banded fertilizer on the surface or 2 inches deep.

On the other hand, Jacques (1943) found in New Zealand that with

reseeded pastures subsurface placement of superphosphate to a depth of 6 inches gave greater root growth in the subsurface layers than did surface application. Although the surface application was superior in the early stages of growth, the subsurface application led to greater yields later in the season, especially in late spring and early summer. He concludes "that over the season as a whole the surface roots of grasses (weight for weight) were less effective than the deep-seeded ones in procuring food, even where the fertilizer was concentrated in a layer for them, and despite the somewhat better initial growth in the establishment period."

From the preceding considerations, it is evident that the comparative effectiveness of subsurface and surface applications of phosphate must be further evaluated for a wide variety of soil and moisture conditions before it can be predicted which method or combination of methods will be most satisfactory under various conditions.

V. Utilization of Subsoil Phosphorus

The possible importance of subsoil phosphorus and other nutrients in the nutrition of crop plants and in determining the need for and efficient use of fertilizers has long been recognized. Recently, Bradfield (1946) and Winters and Simonson (1951) have called attention to the tremendous potential reserves of nutrient elements in subsoils and the importance of making better use of these reserves through improved methods of soil management.

Although the various factors affecting the utilization of subsoil phosphorus by crop plants are much the same as those affecting the phosphorus in surface soils, their relative importance is quite different. Such factors as soil structure, aeration, drainage, and the root distribution of plants—all factors which affect either positional or physiological availability—assume much greater importance. Moreover, these factors and their interrelationships have been more difficult to evaluate than under surface soil conditions. It is partly because of this situation that our knowledge of the contribution of subsoil nutrients to the growth of crops on different soils is so meager. There is some evidence that, on certain well-drained permeable soils, deep-rooted crops may be able to get considerable quantities of nutrient elements from lower horizons (Weaver, Jean, and Crist, 1922; Robertson and Stewart, 1935; Crowther, 1935). On the other hand, it has been observed that, on soils of poor structure and drainage, root growth and activity may be so limited, even in subsurface horizons, that fertilizer applied at the bottom of the plow furrow may be ineffective because of poor soil aeration and limited root development (Hoffer, 1945a, 1945b). Between these

two extremes, it is evident that there is a wide range of subsoil conditions about which little is known regarding the availability of the native phosphorus and the possibilities of adding phosphate fertilizers by deep placement.

The more important questions that need to be answered in evaluating the role of subsoil phosphorus in crop production are the following:

1. What are the amounts and the availability of the phosphorus compounds in the subsoils of different soil types? And how do these affect the fertilizer needs in different cropping systems? It is obvious that if plants can get appreciable amounts of phosphorus from subsoils, soil testing which involves only surface soil samples cannot give an adequate estimate of phosphorus fertilizer needs. Closely related is the question as to the availability of the native phosphorus in exposed subsoils, and the extent to which phosphorus fertilizers may be needed in improving their fertility and in improving badly eroded soils.

2. What is the feasibility of adding phosphorus fertilizers to subsoils, not only as a means of supplementing surface soil applications, but also as a means of obtaining deeper penetration of plant roots?

3. To what extent can management practices affect the availability and utilization of subsoil phosphorus or that added to subsoils in fertilizers?

As discussed in Chapter XIII, the depth distribution of total, organic, and dilute acid-soluble phosphorus varies greatly in different soils. In many soils one or more of the lower horizons or parts of horizons are higher in total phosphorus than the surface. In some soils this is related to the increase in clay content with depth, but in many cases large amounts are found in the C horizons where there has been no accumulation of clay. A minimum often is found in the lower A and upper B horizons where the dilute acid-soluble phosphorus is likewise very low. Significantly, the lower B and C horizons in some soils contain much higher amounts of dilute acid-soluble phosphorus than does the surface. Pearson *et al.* (1940) found, for example, that an average of about 25 per cent of the total phosphorus in the C horizon of soils derived primarily from loess was soluble in 0.002 *N* H_2SO_4, as contrasted to about 2.5 per cent in the surface soil and to only about 1 per cent in the sub-surface zone of minimum total phosphorus content.

1. Availability of Subsoil Phosphorus

The availability of subsoil phosphorus, however, cannot be determined from solubility data alone, for recent work has shown that the relationship between plant availability and solubility of subsoil phosphorus is very poor, at least under certain conditions (Thornton, 1935;

Stelly, 1942). Because of this, and because of difficulties involved in determining the plant availability of subsoil nutrients under field conditions, most of the information that has been obtained is with horizon samples in greenhouse pot tests. In general, these studies show that the lower A and upper B horizons of the soils of the humid region are ordinarily much more deficient in phosphorus than the surface soil (Thornton, 1935; Rost, 1940; Stelly, 1942). On the other hand, Stelly (1942) found that the availability of the phosphorus in the lower B and C horizons of certain soils may be greater than that in surface soils and especially greater than that in the B_1 horizons. This is evident from the data in Tables III and IV. Alfalfa made as good or better growth with-

TABLE III

CROP RESPONSE TO PHOSPHATE FERTILIZER ON HORIZONS OF TAMA SILT LOAM[a]

Horizon and pH	*Depth, inches*	*Soluble[b] P* *p.p.m.*	*Yield, grams/pot*			
			Sudan grass		*Alfalfa*	
			No P	*P[c]*	*No P*	*P[c]*
A_1, pH 5.2	0–6	8	13.8	19.9	7.9	10.7
B_1, pH 5.5	13–18	7	0.5	5.6	1.3	8.1
B_3, pH 5.5	24–32	32	1.2	4.5	5.6	8.3
C_1, pH 5.8	36–45	106	2.8	5.3	7.1	8.4
C, pH 5.9	48–54	184	3.4	7.4	7.2	7.7

[a] Stelly (1942).

[b] Soluble P refers to solubility in 0.002 *N* H_2SO_4 (Truog method).

[c] Superphosphate applied at rate of 400 pounds per acre to Sudan grass, and 200 pounds per acre to following crop of alfalfa.

TABLE IV

RESPONSE OF CROPS TO PHOSPHATE FERTILIZATION ON HORIZONS OF WELLER SILT LOAM[a]

Horizon and pH	*Depth, inches*	*Soluble[b] P* *p.p.m.*	*Yield, grams/pot*			
			Corn		*Alfalfa*	
			No P	*P[c]*	*No P*	*P[c]*
A_2, pH 5.4	1½–6	5	10	26	2.9	8.7
$B_{22,3}$, pH 4.4	28–34	43	20	35	1.8	3.5
C, pH 5.0	49–54	153	43	52	5.6	4.9

[a] Stelly (1942).

[b] Soluble P refers to solubility in 0.002 *N* H_2SO_4 (Truog method).

[c] $CaH_4(PO_4)_2$ added at rate equivalent to 240 pounds P_2O_5 for corn and 120 pounds P_2O_5 for alfalfa, the following crop.

out phosphorus fertilizer on the C horizons as on the surface soils, and the C horizons showed little or no need for phosphorus fertilizer. In contrast, the yield of Sudan grass on these horizons was more than doubled by the addition of phosphorus, even though they contained nearly 200 p.p.m. of acid-soluble phosphorus.

On similar soils derived from more acid loess, however, where the pH value of the C horizon is about 5.0, compared with 6.7 and 5.9 for the Grundy and Tama soils, respectively, the phosphorus was found to be readily available to non-legumes. The yield of corn without phosphate, for example, was over four times as much on the C horizon of Weller silt loam as on the surface soil, and the response to phosphate fertilizer was only about 10 per cent as large as on the surface soil. It seems evident, therefore, (a) that the different horizons of a given soil may range from very deficient to well-supplied with plant-available phosphorus, and (b) that the availability of phosphorus in subsoil horizons varies widely with the type of crop grown.

The question that is unanswered, of course, is whether the subsoil phosphorus that is available to plants in pot tests in the greenhouse is available under undisturbed field conditions. There is not only the problem of physiological availability, which in subsoils is largely related to aeration and moisture conditions, but also that of positional availability. It is well established that very low concentrations of oxygen or high concentrations of carbon dioxide in the substrate reduces root respiration and may reduce the uptake of nutrient ions by the roots of many crop plants. The importance of these factors on plant nutrition in general has been discussed in recent excellent reviews by Page and Bodman (1951) and Russell (1952). Winters and Simonson (1951) have also presented an excellent review of the nature and properties of subsoil layers and the relationships of subsoils to plant growth.

The positional availability of the phosphorus in subsoil horizons is determined largely by (a) the type of root system, (b) the location of the horizon containing available phosphorus and its general suitability for root development, and (c) the character of the horizons above it. That the roots of some crops penetrate to great depths in permeable soils is well known (Weaver, 1926). Few quantitative data are available, however, on the comparative development of plant roots and their absorption of nutrients as related to the physical and chemical characteristics of the soil horizons. The recent excellent investigations of Weaver and Darland (1949) point the way to much-needed work. In their comprehensive study on 33 monoliths of 16 soil types in Nebraska and Kansas, these investigators found marked effects of different soil horizons on the character and distribution of the roots of 11 species of native grasses

The presence of claypans greatly reduced root penetration, but even in compact B horizons of some of these soils they found considerable root penetration not only between the structural units but also through them. In a Crete silty clay loam, a claypan soil, for example, a marked branching and large proportion of the root system were found in the mellow loessial C horizon below the 18- to 28-inch compact B horizon. Although the favorable physical conditions in the C horizon are probably largely responsible, it is possible that the higher content of dilute- acid-soluble phosphorus in this horizon than in the B_1 previously referred to (Pearson *et al.*, 1940; Lipps and Chesnin, 1950) may be partly responsible.

2. *Management Practices Affecting Utilization of Phosphorus in Subsoils*

Although the factors affecting the availability of subsoil phosphorus are incompletely understood, it seems probable that in some soils at least the utilization of some of the vast reserves of subsoil phosphorus through improved management practices or the incorporation of phosphorus in the subsoil in fertilizers offers real promise for more efficient crop production.

a. Deep Tillage. Any practices that increase root penetration through improved aeration, such as deep tillage or drainage, should make possible greater utilization of subsoil phosphorus. Subsoiling has often been advocated on claypan soils as a means of improving crop growth. In general, the results have not been encouraging (Winters and Simonson, 1951), but it must be recognized that this may be due to inadequate machinery for such operations or to a failure to recognize other factors. Where the compact horizons may be very deficient in certain nutrient elements, it is possible that a combination of subsoiling and fertilization would be more effective in promoting deeper rooting and making more phosphorus available from lower horizons. Data by Tiedjens (1948) and Woodruff and Smith (1946) indicate possibilities of this combination.

b. Deep-Rooted Crops. The growing of deep-rooted legume crops in the crop rotation may be the most effective means not only of getting greater utilization of subsoil phosphorus by the crop in question but also of making more phosphorus available to other crops in the rotation. This has been emphasized by DeTurk (1942). He found that on some of the Illinois experimental fields the regular use of sweet clover and limestone in the rotation materially increased the available phosphorus in the surface soil. He believed that this was due to the upward transfer of phosphorus from the subsoil by sweet clover, although it is evident that other factors also may have been involved. Deep-rooted crops such

as alfalfa and sweet clover may also benefit the following crops by improving subsoil structure and aeration.

The recent trend toward increased use of alfalfa and brome grass in place of red clover and timothy in crop rotations in certain sections of the country may, therefore, be quite significant. As shown recently by Lambda, Ahlgren, and Muckenhirn (1949), the percentage of the total root growth of alfalfa and of brome grass below the 16-inch soil depth was five to ten times greater than that of red clover and timothy.

c. Subsoil Fertilization. Subsoil applications of phosphorus fertilizer may be feasible from several standpoints. As previously indicated, many soils have very low amounts of available phosphorus in the horizons immediately below the surface (A_2 and upper B horizons) even though they may contain large amounts in lower horizons. Is it feasible to apply phosphorus to such deficient horizons, not as a substitute for surface soil applications, but as a means of increasing root penetration, reducing drought hazards, or increasing the availability of other nutrients? It is a well-established fact that the application of fertilizers in a nutrient-deficient subsoil zone increases the concentration of roots within that zone. There is some evidence that this may be at the expense of their development both in the upper and deeper soil layers (Sokolov, 1937; Ferrant and Sprague, 1940), but the recent interesting studies of Marsh *et al.* (1952) indicate that this is not serious. On the other hand, they found that the placement of phosphorus and nitrogen fertilizer below an undisturbed core of impermeable subsoil resulted in the profuse development of sunflower roots in this relatively impermeable core above.

Militating against the practice of subsoil fertilization is the practical difficulty of applying fertilizer at considerable depths (Volk, 1947). Nevertheless, the practice of subsoil fertilization with phosphorus is worthy of investigation under certain soil and cropping conditions. An example of such a possibility is the application of rock phosphate or some relatively insoluble phosphorus in the subsurface of very deficient, acid podzolic or prairie soils in combination with soluble phosphate in the well-limed surface layer. The acid conditions and possibly more favorable moisture conditions of the subsurface layer should make the rock phosphate slowly available and help promote crop growth, especially that of perennial leguminous crops.

As a basis for making fuller use of subsoil phosphorus or that applied to subsoils in fertilizers, there is a great need for more information: first, regarding the character and downward distribution of the roots of various crops on different soil types as influenced by the physical and chemical properties of the soil horizons; and second, on the amounts of

phosphorus that can be absorbed by plants from the undisturbed soil. Although such work is difficult, the new technique using soil monoliths proposed by Weaver and Darland (1949) and especially the tracer technique recently utilized by Hall (1951) and Lott, Satchell, and Hall (1950) in tracing root distribution and activity should make possible much more rapid progress than in the past.

VI. Efficient Phosphate Use in Relation to Other Factors

As previously mentioned, management practices may indirectly affect efficient phosphorus use, either by altering the physical properties of soils or by providing other nutrients needed for maximum plant growth. Among those relating to soil physical properties, the most important are drainage, irrigation, tillage, and cropping practices. They exert their influence on phosphorus utilization largely through their effect on soil moisture and aeration. In recent years there has been a much better recognition of these factors in plant nutrition, and several good reviews have been published on this subject (Wadleigh and Richards, 1951; Page and Bodman, 1951; and Russell, 1952).

1. Soil Moisture

The higher the moisture content of soils within the range up to the optimum supply, the more readily available the phosphorus is to plants. This is indicated by the phosphorus content of plants grown on irrigated and nonirrigated soils (Greaves and Nelson, 1925; Emmert, 1936; Thomas *et al.*, 1942; Haddock, 1952). Likewise, several investigators have found that the phosphorus content of plants is lower in a dry than a wet season, whereas the reverse is true for nitrogen (Daniel and Harper, 1935; Smith and Simpson, 1950; Snider, 1945). The cause for the decreased absorption of phosphorus from soils of low moisture content is not known, but it may be ascribed in part to an increase in phosphorus fixation, as suggested by Trumble (1947) and Wadleigh and Richards (1951). From the practical standpoint, it emphasizes the importance of adequate moisture especially in the zone of fertilizer incorporation. It is true that plant roots can absorb some phosphorus from soils at or near the wilting point (Hunter and Kelley, 1946; Volk, 1947) if some of the roots are in moist soil, but the amounts thus absorbed are very small and cannot provide for the needs of an actively growing crop.

Poor drainage or excess of soil mosture, on the other hand, will materially reduce phosphate absorption. This may be due to reduced aeration and to less root penetration, two indirect factors previously referred to. It may also be due to reduced phosphorus availability in

the soil. Paul and DeLong (1949) found that prolonged flooding reduced the amount of easily soluble phosphorus, especially in the presence of easily decomposable organic matter. They obtained evidence that this was due to the enhanced activity of the sesquioxide fraction in the soil caused by reducing conditions. Hester and Shelton (1947) had earlier obtained similar evidence and concluded that fixation by the sesquioxides, activated by the reducing conditions, may be the explanation for the extreme phosphorus deficiency often observed in heavy soils after wet, cold springs or waterlogging. This may also explain the marked phosphorus deficiencies found in poorly drained, irrigated mountain meadow soils in the Western States (Thorne, 1952, private communication). For several reasons, therefore, good drainage means better utilization of native or applied phosphates.

2. Nutrient Deficiencies

Deficiencies of other nutrients may also greatly effect the efficient utilization of phosphorus. This principle has been more fully recognized in recent years. Some striking effects of adequate nitrogen fertilization on the efficiency of applied phosphorus have recently been reported (Coleman, 1944; Dumenil and Nelson, 1948; Smith *et al.*, 1950). As an example, some results of Dumenil and Hanway (1952) are shown in Table V. Phosphorus fertilizer alone gave no increases in corn yields,

TABLE V

EFFECT OF NITROGEN AND POTASSIUM ON RESPONSE OF CORN TO PHOSPHATE FERTILIZATION AND ON PHOSPHORUS CONTENT OF THE CORN LEAF[a,b]

	Without K		*With K*	
Treatment	*Yield, bushels/acre*	*% P, leaf*	*Yield, bushels/acre*	*% P, leaf*
None	46.1	0.20	47.1	0.20
N	65.5	0.22	65.2	0.22
P	46.6	0.22	38.5	0.20
NP	75.7	0.28	88.2	0.27

[a] Dumenil and Hanway (1952).

[b] N, P_2O_5, and K_2O applied at rates of 60 pounds per acre in ammonium nitrate, superphosphate, and muriate of potash, respectively.

but where adequate amounts of nitrogen had been applied the increased yield was 10.2 bushels, and where both nitrogen and potassium were applied the increased yield from phosphorus was 23 bushels. Of interest also was the phosphorus content of the leaves. Phosphorus alone had no effect on the percentage phosphorus in the leaves, but the combina-

tion of phosphorus and nitrogen increased it from 0.22 to 0.28 per cent. Bennett, *et al.* (1953) have also found that nitrogen fertilization may increase the phosphorus content of corn leaves. The reason for this effect is not clear, but part of the explanation may be the effect of nitrogen in increasing root growth and the foraging power of the roots for phosphorus.

The use of phosphorus fertilizers may likewise result in greater utilization of the soil phosphorus by crops on phosphorus-deficient soils (Spinks *et al.*, 1948; Larsen, 1952; Strzemienski, 1948). Strzemienski found through use of P^{32}, for example, that on two phosphorus-deficient soils from New Zealand, plants that received phosphorus fertilizer took up three to eight times as much soil phosphorus as did the controls. According to Dion *et al.* (1949), who likewise used P^{32} in their studies, a greater uptake of soil phosphorus is likely to occur when small amounts of fertilizer are used, but a lower soil phosphorus uptake when large amounts are applied.

VII. General Conclusions

In conclusion, it may be well to emphasize that the efficient use of fertilizers must, of course, be based first of all on the soil and crop requirements, as discussed in other chapters of this monograph. The improvement and greater use of soil testing methods represents an important step forward in obtaining efficient utilization of phosphorus fertilizers. (See Chapter VI.) Moreover, the need of taking into consideration not only the individual crops in the rotation but the rotation as a whole in determining the fertilizer program is becoming more fully recognized.

Behind all soil management and farming practices are the economic considerations. These must, of course, be based on quantitative data. Moreover, principles established in the research laboratory need to be more fully evaluated in the field for a wide range of soil conditions, cropping systems, and management practices. It is not enough to have average values.

Many of the soil management practices discussed in this chapter relate to the problem of phosphorus fixation. Much has been accomplished in recent years in an understanding of this phenomenon, but the problem is still far from being solved, especially in its application to field conditions. The time factor in fixation must be more fully evaluated and more consideration should be given to the residual effects of phosphorus fertilizers. The goal in efficient fertilizer use is not necessarily a high total phosphorus content in our soils, but rather an adequate revolving fund of plant-available phosphorus. This will require

a much greater use of phosphate fertilizers on most farms than in the past, but it also involves adoption of all soil and crop management practices that will help keep the revolving fund adequate to meet the needs of high-yielding crops.

References

Aslander, A. 1950. The availability of phosphates after standard fertilization. *Trans. 4th Intern Congr. Soil Sci.* **2**: 158–163.

Barbier, G., Maroger, M., and Gachon, L. 1951. Acide phosphorique et humus. *Ann. Agron.* **2**: 317–333.

Bauer, F. C., and Nelson, J. L. 1951. Residual value of phosphates in permanent fertility plots. Unpublished data. Illinois Agricultural Experiment Station.

Bennett, W. F., Stanford, G., and Dumenil, L. C. 1953. Effects of nitrogen fertilization on yield and on the nitrogen, phosphorus, and potassium content of the corn leaf and grain. *Soil Sci. Soc. Amer. Proc.* **17**: (In press).

Blaser, R. E., and McAuliffe, C. 1949. Utilization of phosphorus from various fertilizer materials: I. Orchard grass and Ladino clover in New York. *Soil Sci.* **68**: 145–150.

Boischiot, P., and Sylvester, P. 1949. Solubilisation de l'acide phosphorique dans les soils calcaires. *Compt. rend.* **229**: 596–598.

Bower, C. A. 1945. Unpublished data. Iowa Agricultural Experiment Station.

Bradfield, R. 1946. Where are the discoveries in soil science leading. I. The physical chemistry of soil-plant relationships. *Soil Sci. Soc. Amer. Proc.* **11**: 3–8.

Bradley, D. B., and Sieling, D. H. 1953. Effect of organic substances on phosphate precipitation by iron and aluminum as influenced by pH. II. Anions and sugars. *Soil Sci.* (In press).

Brown, L. A. 1935. A study of phosphorus penetration and availability in soils. *Soil Sci.* **39**: 277–287.

Bushnell, J. 1950. Fertilizers for early cabbage, tomatoes, cucumbers, and sweet corn. *Ohio Agr. Expt. Sta. Research Bull.* **697**.

Caldwell, A. C., Hustrulid, A., and MacGregor, J. M. 1951. The uptake and recovery of phosphorus applied broadcast to established stands of alfalfa. Unpublished data. Minnesota Agricultural Experiment Station.

Chaminade, R. 1943. Sur l'existence dans les sols de complexes phospho-humiques. *Compt. rend. acad. agr. France* **29**: 235–237.

Chaminade, R., and Blanchet, R. 1952. Influence de l'humus sur la nutrition minérale de la plante dans le sol. *Compt. rend.* **234**: 878–879.

Chaminade, R., and Vistelle, R. 1947. Influence de l'humus sur la fixation et la mobilité de l'acide phosphorique dans les sols. *Ann. agron.* **17**: 536–544.

Coe, D. G. 1926. The effects of various methods of applying fertilizers on crop yields. *Soil Sci.* **21**: 127–141.

Coleman, R. 1944. The effect of nitrogen upon the response of cotton and oats to phosphorus. *J. Am. Soc. Agron.* **36**: 970–975.

Converse, C. D. 1948. Phosphorus fertility and movement studies on newly reclaimed sandy soils. *Soil Sci. Soc. Amer. Proc.* **13**: 423–427.

Cook, R. L. 1938. The effect of fertilizer placement on the yield of herbage in permanent pasture in 1938. *Proc. Natl. Joint Comm. Fertilizer Application, 14th Ann. Meeting*, pp. 125–127.

Cook, R. L. 1951. Fertilizers for legumes. Unpublished data. Michigan State College.

Copeland, O. L., and Merkle, F. G. 1942. The influence of certain soil treatments

upon the fixation and availability of applied phosphates. *Soil Sci. Soc. Amer. Proc.* **6**: 321–327.

COSPER, H. R., RHOADES, H. F., and KOEHLER, F. E. 1951. Evaluation of the phosphorus status of old rotation plots at the Scottsbluff Substation by the use of "A" values. Unpublished data. Nebraska Agricultural Experiment Station and U. S. Department of Agriculture.

CROWTHER, E. M. 1935. Subsoil structure and crop nutrition. *Trans. 3rd Intern. Congr. Soil Sci.* **3**: 126–139.

CROWTHER, E. M., and YATES, F. 1941. Fertilizer policy in war-time: The fertilizer requirements of arable crops. *Empire J. Exptl. Agr.* **9**: 77–97.

DALTON, J. D., RUSSELL, G. C., and SIELING, D. H. 1952. Effect of organic matter on phosphate availability. *Soil Sci.* **73**: 173–181.

DANIEL, H. A., and HARPER, H. J. 1935. The relation between effective rainfall and total calcium and phosphorus in alfalfa and prairie hay. *J. Am. Soc. Agron.* **27**: 644–652.

DETURK, E. E. 1942. The problem of phosphate fertilizers. *Illinois Agr. Expt. Sta. Bull.* **484**.

DION, H. G., SPINKS, J. W. T., and MITCHELL, J. 1947. Experiments with radio-phosphorus on the uptake of phosphorus by wheat. *Sci. Agr.* **29**: 167–172.

DODD, D. R. 1938. Fertilizer placement experiments with permanent pastures. *Proc. Natl. Joint Comm. Fertilizer Application, 14th Ann. Meeting*, pp. 120–123.

DODD, D. R. 1951. Grass roots on surface respond quickly to topdressing meadows and pastures. *Ohio Farm and Home Research*, **36**(273): 88–89, 93.

DODD, D. R. 1951. Report of pasture survey. Unpublished data. Ohio State University.

DRAKE, M., and STEWART, E. H. 1950. Alfalfa fertility investigations in South Carolina. *Soil Sci.* **69**: 459.

DULEY, F. L. 1930. Methods of applying fertilizers to wheat. *J. Am. Soc. Agron.* **22**: 515–521.

DUMENIL, L. C., and HANWAY, J. 1952. Unpublished data. Iowa Agricultural Experimental Station.

DUMENIL, L. C., and NELSON, L. B. 1948. Nutrient balance and interaction in fertilizer experiments. *Soil Sci. Soc. Amer. Proc.* **13**: 335–341.

EMMERT, E. M. 1936. Effect of drought on the nutrient levels in the tomato plant. *Soil Sci.* **41**: 67–70.

FERGUS, E. N., and THAXTON, R. M. 1952. Unpublished data. Kentucky Agricultural Experiment Station.

FERRANT, N. A., and SPRAGUE, H. B. 1940. Effect of treating different horizons of Sassafras loam on root development of red clover. *Soil Sci.* **50**: 141–161.

FRIED, M., and DEAN, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

FULLER, W. H., and DEAN, L. A. 1949. Utilization of phosphorus from green manures. *Soil Sci.* **68**: 197–202.

FULLER, W. H., and ROGERS, R. N. 1951. Utilization of phosphorus from barley residues in calcareous soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **123**.

GAARDER, T., and GRAHL-NIELSON, O. 1935. Die Bindung der Phosphorsäure im Erdboden. II. Untersuchungen aus Westnorwegen. *Vestlandets Forstlige Forsoks-station Meddel*, **18**.

GERRETSEN, F. C. 1948. The influence of microorganisms on the phosphate intake by the plant. *Plant and Soil* **1**: 51–81.

GREAVES, J. E., and NELSON, D. H. 1925. The influence of irrigation water and manure on the composition of the corn kernel. *J. Agr. Research* **31**: 183–189.

HADDOCK, J. L. 1952. The influence of soil moisture conditions on the uptake of phosphorus from calcareous soils by sugar beets. *Soil Sci. Soc. Amer. Proc.* **16**: 235–238.

HALEY, L. E. 1951. The effect of deep placement of phosphorus on native bluegrass pasture. M. S. thesis, Purdue University, Lafayette, Indiana.

HALL, N. S. 1951. Studies of root distribution of different crops through the use of radiophosphorus and its relation to fertilizer placement. Unpublished data. North Carolina Agricultural Experiment Station.

HAYNES, J. L., and THATCHER, L. E. 1950. Band seeding method for meadow crops. *Ohio Farm and Home Research* **35**: 3–5.

HERVEY, R. J., KAPP, L. C., JOHNSTON, J. R., and SMITH, J. C. 1950. Use of sweet clover for deep placement of phosphorus. *Soil Sci. Soc. Amer. Proc.* **15**: 258–262.

HESTER, J. B., and SHELTON, F. A. 1937. Soil organic matter investigations upon costal plain soils. *Virginia Truck Expt. Sta. Bull.* **94**: 1397–1428.

HESTER, J. B., and SHELTON, F. A. 1947. Solubility of iron in submerged soils. *Science* **106**: 595–596.

HINES, R. C., JR. 1951. Subsurface placement of fertilizer in sod crops. Unpublished data. Tennessee Valley Authority, Knoxville, Tennessee.

HOFFER, G. N. 1945a. Fertilized corn plants require well-ventilated soils. *Better Crops with Plant Food* **29**: 6–9.

HOFFER, G. N. 1945b. Some whys and wherefores for air-conditioning soils. *Better Crops with Plant Food* **29**: 19–21, 49–50.

HUNTER, A. S., and KELLEY, O. J. 1946. A new technique for studying the absorption of moisture and nutrients from soil by plant roots. *Soil Sci.* **62**: 441–450.

JACKSON, M. L., ATTOE, O. J., STAROSTKA, R. W., TAMURA, T., and KAUFMAN, A. 1950. Phosphorus utilization by oats and corn as influenced by carrier compound and placement, measured with P^{32}. Unpublished data. Wisconsin Agricultural Experiment Station.

JACQUES, W. A. 1943. Root-development in some common New Zealand pasture plants. II. Perennial rye-grass (*Lolium perenne*), cocksfoot (*Dactylis glomerata*). and white clover (*trifolium repens*). Effect of fertilizer placement on the yield of roots and herbage. *New Zealand J. Sci. Tech.* **25A**: 91–117.

JENSEN, C. A. 1917. Effect of decomposing organic matter on the solubility of certain inorganic constituents of the soil. *J. Agr. Research* **9**: 253–268.

KAILA, A. 1949. Biological absorption of phosphorus. *Soil Sci.* **68**: 279–289.

KUBOTA, J., RHOADES, H. F., and HARRIS, L. 1947. Effects of different cropping and manurial practices on some chemical properties of an irrigated Chestnut soil. *Soil Sci. Soc. Amer. Proc.* **12**: 304–309.

LAMBDA, P. S., AHLGREN, H. L., and MUCKENHIRN, R. J. 1949. Root growth of alfalfa, medium red clover, bromegrass, and timothy, under various soil conditions. *Agron. J.* **41**: 451–458.

LARSEN, S. 1952. The use of P^{32} in studies on the uptake of phosphorus by plants. *Plant and Soil* **4**: 1–10.

LARSON, W. E., NELSON, L. B., and HUNTER, A. S. 1952. The effects of phosphate fertilization upon the yield and composition of oats and alfalfa grown on phosphate-deficient soils. *Agron. J.* **44**: 357–361.

LAWTON, K., ROBERTSON, L. S., COOK, R. L., and ROOD, P. J. 1947. A study of correlation between rapid soil tests and response of legume hay to phosphorus and

potassium fertilization on some Michigan soils. *Soil Sci. Soc. Amer. Proc.* **12**: 353–358.

LEWIS, G. C., BAKER, G. O., and SNYDER, R. S. 1950. Phosphate fixation in calcareous soils. *Soil Sci.* **69**: 55–62.

LEWIS, A. H., and STRICKLAND, A. G. 1944. The placement of fertilizers. II. Cereals. *J. Agr. Sci.* **34**: 73–75.

LIPPS, R. C., and CHESNIN, L. 1950. The phosphorus status of some azonal, prairie, and Chernozem soils in eastern Nebraska. *Soil Sci. Soc. Amer. Proc.* **15**: 329–333.

LOTT, W. L., SATCHELL, D. P., and HALL, N. S. 1950. A tracer-technique in the study of root extension. *Proc. Am. Soc. Hort. Sci.* **55**: 27–34.

LYONS, E. S., RUSSEL, J. C., and RHOADES, H. F. 1944. Commercial fertilizers for the irrigated sections of western Nebraska. *Nebraska Agr. Expt. Sta. Bull.* **365**.

MARSH, A. W., SWARNER, L. R., TILESTON, F. M., BOWER, C. A., and HOFFMAN, E. N. 1952. Irrigation management investigations on nonsaline soils. *Oregon Agr. Expt. Sta. Tech. Bull.* **23**.

MCAULIFFE, C., and BRADFIELD, R. 1952. Utilization of phosphorus in farm manure: III. The uptake of phosphorus by Sudan grass from manure and superphosphate when incorporated into the soil at different depths. Unpublished manuscript. Department Agronomy, Cornell University, Ithaca, New York.

MCAULIFFE, C., PEECH, M., and BRADFIELD, R. 1949. Utilization to plants of organic and inorganic forms of phosphorus in sheep manure. *Soil Sci.* **68**: 185–196.

MCAULIFFE, C., STANFORD, G., and BRADFIELD, R. 1951. Residual effects of phosphorus in soil at different pH levels as measured by yield and phosphorus uptake by oats. *Soil Sci.* **72**: 171–178.

MCGEORGE, W. T. 1939. Factors influencing the availability of native soil phosphate and phosphate fertilizers in Arizona soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **82**.

MCGEORGE, W. T., and BREAZEALE, J. F. 1936. Fertilization of alfalfa on alkaline calcareous soils. *Arizona Agr. Expt. Sta. Bull.* **154**.

MCGEORGE, W. T., and GREENE, R. A. 1935. Oxidation of sulphur in Arizona soils and its effect on soil properties. *Arizona Agr. Expt. Sta. Tech. Bull.* **59**.

MIDGLEY, A. R. 1931. The movement and fixation of phosphates in relation to permanent pasture fertilization. *J. Am. Soc. Agron.* **23**: 788–798.

MIDGLEY, A. R., and DUNKLEE, D. E. 1945. The availability to plants of phosphates applied with cattle manure. *Vermont Agr. Expt. Sta. Bull.* **525**.

MOSER, F. J. 1942. Influence of leguminous plant additions on the organic matter content and available nutrient supply of southern soils. *J. Am. Soc. Agron.* **34**: 711–729.

MULVEY, R. R., CUMINGS, G. A., and SCHOENLEUER, L. G. 1938. Fertilizer placement experiment on pasture. *Proc. Natl. Joint Comm. Fertilizer Application, 14th Ann. Meeting*, pp. 125–127.

NELSON, W. L., KRANTZ, B. A., and WELCH, C. D., and HALL, N. S. 1949. Utilization of phosphorus as affected by placement: II. Cotton and corn in North Carolina. *Soil Sci.* **68**: 137–144.

NELSON, L. B., MELDRUM, H. R., and PIERRE, W. H. 1946. Fertilizer needs of legume hays in Iowa. *Proc. Natl. Joint Comm. Fertilizer Application, 22nd Ann. Meeting*, pp. 20–23.

NIELSEN, K. F. 1952. The influence of alfalfa green manure on the availability of phosphorus to plants. Ph.D. thesis, Ohio State University, Columbus, Ohio.

NORUM, E. B., and YOUNG, R. A. 1950. Effect of rate, method of application, and

source of phosphate fertilizers on yield of wheat and durum. *North Dakota Agr. Expt. Sta. Bimo. Bull.* **12**: 125–128.

OLSEN, S. R., SCHMEHL, W. R., WATANABE, F. A., SCOTT, C. O., FULLER, W. H., JORDAN, J. V., and KUNKEL, R. 1950. Utilization of phosphorus by various crops as affected by source of material and placement. *Colorado Agr. Expt. Sta. Tech. Bull.* **42**.

PAGE, J. B., and BODMAN, G. B. 1951. The effect of soil physical properties on nutrient availability. *In* Mineral Nutrition of Plants. pp. 133–166. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

PAPADAKIS, J. S. 1947. Experiments on the immobilization of phosphorus. *Soil Sci.* **64**: 356–369.

PAUL, H., and DELONG, W. A. 1949. Phosphorus studies: I. Effects of flooding on soil phosphorus. *Sci. Agr.* **29**: 137–147.

PEARSON, R. W., SPRY, R., and PIERRE, W. H. 1940. The vertical distribution of total and dilute-acid soluble phosphorus in twelve Iowa soil profiles. *J. Am. Soc. Agron.* **32**: 683–696.

PEECH, M. 1945. Nutrient status of soils in commercial potato-producing areas of the Atlantic and Gulf Coast: Part II. Chemical data on the soils. *Soil Sci. Soc. Amer. Proc.* **10**: 245–251.

PESEK, J. T. 1951. Unpublished data. Iowa Agricultural Experiment Station.

PIERRE, W. H. 1938. Phosphorus deficiency and soil fertility. Soils and Men. Yearbook of Agriculture, pp. 377–396. U. S. Department of Agriculture, Washington, D.C.

REITH, J. W. S. 1952. Fertilizer placement for cereal crops. *Empire J. Exptl. Agr.* **20**: 103–114.

REYNOLDS, E. B., and SMITH, J. C. 1946. The effect of fertilizer treatments and dates of sampling on the easily soluble phosphorus in soil. *Soil Sci. Soc. Amer. Proc.* **11**: 198–200.

RHOADES, H. F. 1939. Effect of organic matter decomposition on the solubility and fixation of phosphorus in alkaline soils. *Nebraska Agr. Expt. Sta. Research Bull.* **113**.

RICH, C. I., BLASER, R. E., and OBENSHAIN, S. S. 1952. Utilization of fertilizer phosphorus applied as a top-dressing on pastures and meadows. Unpublished data. Virginia Agricultural Experiment Station.

RICH, C. I., JACKSON, M. L., ATTOE, O. J., and TRUOG, E. 1949. Influence of method of placement of fertilizer at the hill on uptake of phosphorus by corn. Unpublished data. Wisconsin Agricultural Experiment Station.

RICH, C. L., OBENSHAIN, S. S., and MCVICKAR, M. H. 1947. The relation of certain soil phosphorus factors in Dunmore silt loam to fertilizer treatment and crop yields. *Soil Sci. Soc. Amer. Proc.* **12**: 270–274.

ROBERTSON, I. M., and STEWART, A. B. 1935. The effect of the lower layers of typical Scottish soils on the uptake of nutrients by plants. *Trans. 3rd Intern. Congr. Soil Sci.* **1**: 247–249.

ROBINSON, R. R., and GARBER, R. J. 1949. Fertilizer experiments on grasslands in the Northeastern Region. Pennsylvania Agr. Expt. Sta. in cooperation with the Regional Pasture Laboratory. *U. S. Dept. Agr. Bull.* **518**.

ROBINSON, R. R., and PIERRE, W. H. 1938. Response of permanent pastures to lime and fertilizers (1930 to 1936). *West Virginia Agr. Expt. Sta. Bull.* **289**.

ROST, C. O. 1940. The relative productivity of some humid sub-soils. *Soil Sci. Soc. Amer. Proc.* **4**: 281–287.

ROYER, A. E., BERTRAMSON, B. R., and MULVEY, R. R. 1948. Soil fertility levels as influenced by long-time differential fertilization practices. *J. Am. Soc. Agron.* **40**: 685–693.

RUSSELL, M. B. 1952. Soil aeration and plant growth. *In* Soil Physical Conditions and Plant Growth. Agronomy Monograph, Vol. 2, pp. 253–302. Academic Press, New York.

SALTER, R. M., and BARNES, E. E. 1935. The efficiency of soil and fertilizer phosphorus as affected by soil reaction. *Ohio Agr. Expt. Sta. Bull.* **553**.

SALTER, R. M., and SCHOLLENBERGER, C. J. 1939. Farm manure. *Ohio Agr. Expt. Sta. Bull.* **605**: 1–69.

SCARSETH, G. D. 1932. Morphological, greenhouse and chemical studies of the Black Belt soils of Alabama. *Alabama Agr. Expt. Sta. Bull.* **237**.

SCARSETH, G. D. 1943. Plant-tissue testing in diagnosis of the nutritional status of growing plants. *Soil Sci.* **55**: 113–121.

SCHALLER, F. 1941. The downward movement of lime and superphosphate in relation to permanent pasture fertilization. *Soil Sci. Soc. Amer. Proc.* **5**: 162–166.

SELL, O. E., and OLSON, L. C. 1947. The effect of surface applied phosphate and limestone on soil nutrients and pH of permanent pasture. *Soil Sci. Soc. Amer. Proc.* **11**: 238–245.

SIELING, D. H., and STRUTHERS, P. H. 1950. *Massachusetts Agr. Expt. Sta. Bull.* **453**. (Annual Report, 1948–1949, p. 9.)

SMITH, F. W. 1947. The effect of time, rate, and method of application of fertilizer on the yield and quality of hard red winter wheat. *Soil Sci. Soc. Amer. Proc.* **12**: 262–265.

SMITH, J. C., FUDGE, J. F., KAPP, J. E., ADAMS, J. E., PEARSON, R. W., and LEAP, H., JR. 1950. Utilization of fertilizer and soil P by oats and crimson clover as affected by rates and ratios of added N and P_2O_5. *Soil Sci. Soc. Amer. Proc.* **15**: 209–212.

SMITH, A. M., and SIMPSON, K. 1950. Factors affecting the uptake of phosphorus by plants. *J. Sci. Food Agr.* **1**: 208–212.

SNIDER, H. J. 1945. The effectiveness of phosphate fertilization. *Better Crops with Plant Food* **29**: 25–26, 45–48.

SOKOLOV, A. V. 1937. Effect of the distribution of nutritive elements and moisture at different levels in the soil on root development and yield of plants. *Trans Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)* **136**: 203–417.

SPEER, R. J., ALLEN, S. E., MALONEY, M., and ROBERTS, A. 1951. Phosphate fertilizers for the Texas blacklands: I. Relative availability of various phosphatic fertilizers. *Soil Sci.* **72**: 459–464.

SPINKS, J. W. T., DION, H. G., READE, M., and DEHM, J. E. 1948. Study of fertilizer uptake using radiophosphorus. *Sci. Agi.* **28**: 309–314.

STANBERRY, C. O. 1948. The behavior of phosphorus in an alkaline irrigated soil in Washington. *Soil Sci. Soc. Amer. Proc.* **13**: 205–212.

STANFORD, G., and HANWAY, JOHN. 1951. Topdressing legume meadows in Iowa. *Better Crops with Plant Food* **35**: 17–21; 36–37.

STANFORD, G., MCAULIFFE, C., and BRADFIELD, R. 1950. The efficiency of superphosphate top-dressed on established meadows. *Agron. J.* **42**: 423–426.

STANFORD, G., and NELSON, L. B. 1949. Utilization of phosphorus as affected by placement: I. Corn in Iowa. *Soil Sci.* **68**: 129–135.

STEELE, J. G. 1934. The effect of other anions on the retentions of phosphate by colloidal clay. Ph.D. thesis, Ohio State University, Columbus, Ohio.

STELLY, M. 1942. Forms of inorganic phosphorus in the lower horizons of some Iowa soils as indicated by plant availability and chemical methods. Ph.D. thesis, Iowa State College, Ames, Iowa.

STEPHENSON, R. E. 1938. Effect of organic materials and fertilizer treatments upon the soluble nutrients in soils. *Soil Sci.* **45**: 467–475.

STRUTHERS, P. H., and SIELING, D. H. 1950. Effect of organic anions in phosphate precipitation by iron and aluminum as influenced by pH. *Soil Sci.* **69**: 205–213.

STRZEMIENSKI, K. 1948. Soil phosphate uptake as influenced by phosphatic fertilizer. *Nature* **162**: 932.

SWENSON, R. M., COLE, C. V., and SIELING, D. H. 1949. Fixation of phosphate by iron and aluminum and replacement by organic and inorganic ions. *Soil Sci.* **67**: 3–22.

THOMAS, T., MACK, W. B., and COTTON, R. H. 1942. Foliar diagnosis—relation to irrigation. *Proc. Am. Soc. Hort. Sci.* **40**: 531–535.

THORNE, M. D. 1941. Phosphorus fixation by Iowa soils. M.S. thesis, Iowa State College, Ames, Iowa.

THORNTON, S. F. 1935. The available phosphorus and potassium contents of surface soils and subsoils as shown by the Neubauer method and by chemical tests. *J. Am. Soc. Agron.* **27**: 46–51.

TIEDJENS, V. A. 1948. How much lime should we use? *Better Crops with Plant Food* **32**: 17–20, 47–49.

TRUMBLE, H. C. 1947. Some factors affecting the nutrition of herbage plants. *J. Australian Inst. Agr. Sci.*, **13**: 198.

TRUOG, E., ATTOE, O. J., and JACKSON, M. L. 1945. Fertilizer application rationalized. *Soil Sci. Soc. Amer. Proc.* **10**: 219–223.

VOLK, G. W. 1945. Response to residual phosphorus of cotton in continuous culture. *J. Am. Soc. Agron.* **37**: 334–340.

VOLK, G. W. 1947. Significance of moisture translocation from soil zone of low moisture tension to zones of high moisture tension by plant roots. *J. Am. Soc. Agron.* **39**: 93–106.

VOLK, N. J. 1947. Problems connected with subsoil placements of fertilizers. *Proc. Natl. Joint Comm. Fertilizer Application* **23**: 78–86.

WADLEIGH, C. H., and RICHARDS, L. A. 1951. Soil moisture and the mineral nutrition of plants. *In* Mineral Nutrition of Plants. pp. 411–450. E. Truog, Editor. University of Wisconsin Press, Madison, Wisconsin.

WALSH, T., MANNION, L., and RYAN, P. F. 1950. Some aspects of the fertility status of Irish soils. *Trans. 4th Intern. Congr. Soil Sci.* **3**: 111–115.

WEAVER, J. E. 1926. Root Development of Field Crops. McGraw-Hill Book Co., New York.

WEAVER, J. E., and DARLAND, R. W. 1949. Soil-root relationships of certain native grasses in various soil types. *Ecol. Monographs* **19**: 303–338.

WEAVER, J. E., JEAN, F. C., and CRIST, J. W. 1922. Development and activities of roots of crop plants. *Carnegie Inst. Wash. Publ.* **316**.

WEEKS, M. E., and MILLER, H. F. 1948. The residual effects of phosphates used on long-time field experiments. *Soil Sci. Soc. Amer. Proc.* **13**: 102–107.

WELCH, C. D., HALL, N. S., and NELSON, W. L. 1949. Utilization of fertilizer and soil phosphorus by soybeans. *Soil Sci. Soc. Amer. Proc.* **14**: 231–235.

WHITE, J. L., FRIED, M., and OHLROGGE, A. J. 1949. A study of the utilization of phosphorus in green manure crops by the succeeding crop, using radioactive phosphorus. *Agron. J.* **41**: 174–175.

WILLIAMS, E. G. 1950. Phosphate fixation and availability. *J. Sci. Food. Agr.* 1: 244–248.

WILLIAMS, E. G. 1951. Making the best use of phosphate fertilizers. *Scot. Agr.* 31: 68–72.

WINTERS, E., and SIMONSON, R. W. 1951. The subsoil. *Advances in Agron.* 3: 1–92.

WOODRUFF, C. M., and SMITH, D. D. 1946. Subsoil shattering and subsoil liming for crop production on claypan soils. *Soil Sci. Soc. Amer. Proc.* 11: 539–542.

WURSTEN, J. L. 1948. A preliminary report on the relative efficiency of some phosphate fertilizers on some calcareous soils. *Proc. Am. Soc. Sugar Beet Technol. 5th Gen. Meeting.* pp. 308–315.

YUEN, S. H., and POLLARD, A. G. 1951. The availability of soil phosphate: III. The phosphate fixing capacity of soil. *J. Sci. Food Agr.* 2: 260–268.

CHAPTER IX

Liming in Relation to Availability of Native and Applied Phosphates

EMIL TRUOG

I. Introduction

That the rational liming of acid soils promotes the availability of their phosphorus, whether native or added in soluble form, has been maintained by various authorities for many years. Because of space limitations, the relation of liming to the availability of the less-soluble phosphate fertilizers, such as rock phosphate, will not be given more than passing consideration here.

Hilgard (1907), probably more than any other person of his time, stressed the highly favorable influence of lime on the availability of soil phosphorus. He indicated that for best plant growth, sandy soils should contain not less than 0.10 per cent and heavy clay soils not less than 0.60 per cent of lime carbonate, and in general, that 2 to 3 per cent provides optimum conditions. Hilgard was referring, of course, to contents of lime carbonate naturally present and not what might or should be attained through liming of acid soils. Also, his measure of content of calcium carbonate was apparently based on the amount of calcium dissolved by digestion of a soil with HCl of 1.115 sp. gr. He believed that the natural presence of 2 or 3 per cent of calcium carbonate as found by his method, is permissible and even desirable, especially in the case of heavy soils. It is of course now well known that when soils are naturally acid, liming much beyond pH 7, particularly in the case of sandy soils, may, by reducing the availability of minor elements such as boron and manganese, cause a temporary reduction in crop yields. This may be corrected by increasing the supply of these elements through appropriate additions. Thereafter, the full benefit of liming to or near the neutral point may be realized, and legumes, such as alfalfa, may be grown; this by adding organic matter will in time help to alleviate the minor element difficulty.

The truth of the adage, "A lime country is a rich country," is strongly supported by the writings of Hilgard (1907). He gives ex-

amples of soils, which although naturally low in content of phosphorus, have because of a satisfactory content of lime supported a prosperous agriculture. In Wisconsin, one may in many regions pass rather abruptly from soils derived from limestone to soils derived from non-calcareous rocks; in this passage, the change from a vigorous and luxuriant vegetation to one much less so is often most striking. Of course, the greater fertility of the soils derived from limestone is often due not only to a greater lime content but also to a soil of better texture.

The earlier writings dealing with the liming of soils do not mention specifically the influence of this practice on the availability of soil phosphorus. Liebig (1847) states that the favorable influence of liming is due largely to its action in breaking down silicates with consequent liberation of alkalies. Johnston (1849), in his comprehensive and excellent treatise on the use of lime, indicates that the benefits derived from liming arise largely from a neutralization of acids, which in turn favors decomposition of organic matter and liberation of plant nutrients contained therein. He states also that the previous use of lime may lessen the need of phosphate (bones), probably because of the lessened need for the calcium carried by the bones. An increase in availability of native phosphate through liming had as yet not been conceived.

Ruffin (1852), the foremost American authority of his time on liming, discusses at great length the great and varied benefits, particularly neutralization of soil acids, that come from the liming of acid soils; but unfortunately he had no way of knowing that much of the benefit may arise from an increased phosphate availability. In his early marling on his own farm, he experienced some injury to corn as a result of over-marling but states that this was overcome by introducing organic matter through the addition of manure or the growing of grass and legume sod crops. He also states that it is advisable to limit the rate of marl application to that which is needed to neutralize the soil acids present. Since the injury which Ruffin experienced was with corn, and this was overcome by adding organic matter, it appears that a reduction in availability of soil manganese may have been the cause of the injury. Of course, Ruffin had no way of knowing this, but, nevertheless, made the following prophetic statement:

"There are many practices universally admitted to be beneficial; yet there are none of these which are not found sometimes useless, or hurtful, on account of some other attendant circumstance, which was not expected, and perhaps not discovered. Every application of calcareous earth to a deficient soil is a chemical operation on a great scale. Decompositions and new combinations are produced, and in a manner generally conforming to the operator's expectations. But other and un-

known agents may sometimes have a share in the process, and thus cause unlooked-for results. Such differences between practice and theory have sometimes occurred in my use of calcareous manures (as may be observed in some of the reported experiments), but they have neither been frequent, uniform, nor important."

II. Field Experiments

Fortunately extensive and reliable data obtained from field test plots relating directly to the subject of this paper now exist. Probably, by far the best data available in this connection are those obtained by the Ohio Agricultural Experiment Station and reported by Salter and Barnes (1935).

1. Yields with and without Lime

In Table I are given a few of the data reported by Salter and Barnes (1935) dealing with the influence of liming on yields of five crops grown on plots variously treated with N, P, and K, and running continuously for a period of forty years on a field consisting of Wooster and Canfield silt loams. In the beginning the soil had a pH of about 5; the unlimed soil has become somewhat more acid, and the limed soil decidedly alkaline with some free lime carbonate present. Details regarding treatments are given with Table I. The data presented leave no question but that a decided lack of available phosphorus existed in the beginning. Liming, of course, has a favorable influence on many fertility factors which often cannot be precisely distinguished from the favorable influence on phosphate availability. Some of the pertinent points brought out by these data as regards phosphate availability follow:

1. Liming of this strongly acid soil to alkalinity has liberated sufficient native phosphorus for crop use so that with all five crops the percentage yield increases, and also in most cases the direct increases, from phosphorus fertilization have been far less on the limed than on the unlimed plots; also, in the case of corn, clover, and timothy the NKL plots have outyielded the NPK plots (L stands for lime and N, P, and K for elements, as is conventional).

2. During the last 10-year period, yields of corn, clover, and timothy with addition of L to NK plots have been more than double the yields obtained without this addition, and with the other two crops the addition has greatly increased the yields. This again indicates liberation of the native phosphorus by lime.

3. Because yields of all crops on NK plots with L rose during the last 10-year period, and these yields on similarly fertilized plots without

TABLE 1

CROP YIELDS WITH LIME (ALKALINE) AND WITHOUT LIME (pH 5) AND FERTILIZER IN 5-YEAR ROTATION OF CORN, OATS, WHEAT, CLOVER, AND TIMOTHY DURING 40-YEAR PERIOD, 1894–1933, ON SILT LOAM AT WOOSTER, OHIO[a]

		Yield, bushels or pounds per acre			
		Unlimed		*Limed*	
Crop	*Fertilizer treatment*[b]	*Entire 40-year period*	*Last 10-year period*	*Entire 40-year period*	*Last 10-year period*
Corn	None	19.2	11.3	30.7	27.6
	N, K	27.7	18.5	45.3	46.7
	N, K, P	41.9	33.3	55.4	55.6
Oats	None	25.5	20.0	35.2	36.4
	N, K	32.2	27.3	43.0	44.7
	N, K, P	49.6	48.6	52.1	53.6
Wheat	None	9.6	7.4	15.4	16.2
	N, K	12.6	10.6	18.6	19.5
	N, K, P	28.5	28.6	33.2	36.0
Clover	None	948	624	1923	2030
	N, K	1203	732	2393	2559
	N, K, P	2221	1851	3443	3674
Timothy	None	1502	1167	2517	2709
	N, K	1702	1382	2795	3091
	N, K, P	2346	2129	3349	3578

[a] Salter and Barnes (1935).

[b] All fertilizers were applied regularly to corn, oats, and wheat: 24.8 pounds of nitrogen (N) as nitrate of soda, 25.6 pounds of phosphate (P_2O_5) as superphosphate, and 40 pounds of potash (K_2O) to each of these crops.

[c] Limed at the rate of about 2 tons of ground limestone per acre once during each rotation, except during the first 12 years when some burned lime was applied. Limed plots became alkaline, with some free carbonate present; unlimed plots attained a pH of 5 or less.

L dropped markedly during this period, indications are strong that the lime is liberating native phosphorus throughout a long period.

4. That liming will liberate native phosphorus over a long period is further substantiated by the fact that yields with lime alone have been slightly higher during the last 10-year period than throughout the entire period with all crops except corn.

2. *Most Desirable pH*

The pH to which acid soils should be limed for most favorable influence on availability of native and applied phosphates is a question of paramount importance. Here again, data reported by Salter and Barnes

TABLE II

YIELDS WITH AND WITHOUT SUPERPHOSPHATE AT DIFFERENT SOIL REACTIONS IN A 3-YEAR ROTATION OF CORN, SMALL GRAINS, AND LEGUMES ON CANFIELD SILT LOAM DURING 8-YEAR PERIOD, 1926–1933 INCLUSIVE[a]

Soil reaction[b]	*Average yield, bushels or pounds per acre*			
	No phosphate	*With phosphate*[c]	*No phosphate*	*With phosphate*
	Corn		*Oats*	
4.7	15.3	13.6	59.8	70.4
5.2	24.6	28.1	55.1	70.1
5.9	28.6	31.7	55.8	70.8
6.8	35.6	37.8	65.8	69.8
7.4	34.5	32.5	69.3	69.8
	Barley		*Wheat*	
4.7	0.0	0.0	7.7	26.1
5.2	2.8	5.5	11.4	29.2
5.9	10.5	19.3	14.8	34.1
6.8	17.0	22.9	22.2	38.2
7.4	20.7	24.1	27.2	37.9
	Alfalfa		*Sweet clover*	
4.7	157	175	45	30
5.2	623	515	294	170
5.9	1748	1974	1504	2893
6.8	3728	4923	3991	5774
7.4	4691	4813	5320	6270
	Red clover		*Alsike clover*	
4.7	682	572	718	516
5.2	779	863	883	1096
5.9	1355	1832	1537	2792
6.8	2408	3069	2506	3805
7.4	2895	2892	3379	3513
	Timothy		*Soybeans*	
4.7	751	827	1794	1705
5.2	1167	1205	2021	2049
5.9	1299	1758	2029	1984
6.8	2228	2678	2552	2625
7.4	2382	2558	2656	2473

[a] Salter and Barnes (1935).

[b] Soil reaction originally was slightly above pH 5; adjusted lower by addition of sulfur and aluminum sulfate, and higher by addition of ground limestone, amounting to 8 tons for highest pH attained; intended pH values were 4.5, 5.0, 6.0, 7.0, and 8.0.

[c] No manure but P and K at rates per acre as follows were applied: superphosphate (20%), 200 pounds on corn and 400 pounds on small grain on phosphated plots; muriate of potash, 40 pounds on corn and 50 pounds on small grain on all plots.

(1935) provide some of the best evidence available. Some of these data along with soil treatments of the test plots involved are given in Table II. Conclusions which these data appear to support follow:

1. The yields without phosphorus fertilization show in a striking manner that pH 5.9 is not high enough to make notable amounts of native phosphorus available for crop use; in the case of oats, corn, timothy, and soybeans, all of which can tolerate the acidity itself of pH 5.2 without much if any injury, yields did not rise notably in going from pH 5.2 to 5.9, but did rise markedly in going to pH 6.8 and 7.4; in fact, in most cases a rise in pH from 6.8 to 7.4 gave an additional increase in yield.

2. These results show that when this soil had a pH of 5.9 and was low in available phosphorus, liming to near pH 7 increased the yields of six of the ten crops more than did phosphorus fertilization.

3. Indications are that raising the pH of this soil from 6.8 to 7.4 will increase notably the availability of the native phosphorus to most crops, but may cause a slight decrease in the availability of applied phosphorus to some crops.

4. With this soil, maximum availability of both native and applied phosphorus is attained near pH 7, where lime without phosphorus has produced in most cases nearly as large yields as lime with phosphorus.

The results of Salter and Barnes (1935) referred to in this paper accord fully with those obtained in recent years from soil fertility test plots located in Wisconsin on Spencer and Antigo silt loams which are low in available phosphorus. Where the soils have been limed to near pH 7, response from phosphate fertilization has largely vanished except for benefit in starter fertilizer.

3. *Phosphorus Content of Crop*

Since the level of available phosphorus in a soil is usually reflected in the phosphorus content of a crop grown on that soil, another method of revealing the influence of liming or pH on this level of available phosphorus is to determine the phosphorus content of such a crop. This procedure was followed in the case of alfalfa grown on some soil fertility plots of the Wisconsin Agricultural Experiment Station. The soil of these plots is a heavy silt loam, naturally low in available phosphorus and potassium and strongly acid. The pH and fertility levels established and results obtained are given in Table III.

It will be noted that, for the 1949 season, raising the pH from about 5 to near 7 markedly increased the phosphorus content in all cases, indicating that the liming increased the availability of both native and

TABLE III

INFLUENCE OF LIMING ON pH ON AVAILABILITY OF PHOSPHORUS AS REVEALED BY PHOSPHORUS CONTENT OF FIRST CUTTING 2ND-YEAR ALFALFA GROWN ON SPENCER SILT LOAM SOIL FERTILITY PLOTS. ALFALFA CUTTINGS AND pH FIGURES WERE OBTAINED FROM ONE SET OF PLOTS IN 1948 AND ANOTHER IN 1949[a]

Pounds per acre available originally established[b]		*pH of plots harvested*		*Per cent P in alfalfa hay*		*Tons alfalfa hay per acre, 2 cuttings, in 1949*
P	*K*	*1948*	*1949*	*1948*	*1949*	
15	100	5.10	4.89	0.203	0.143	1.14
15	100	6.95	6.71	0.245	0.233	2.03
50	150	5.61	5.23	0.245	0.163	2.26
50	150	6.86	6.89	0.245	0.256	3.85
75	200	5.62	5.21	0.268	0.192	2.91
75	200	6.96	6.90	0.251	0.225	3.85
125	300	5.43	5.37	0.256	0.189	2.95
125	300	6.89	6.92	0.295	0.251	4.12

[a] pH figures and percentages of phosphorus taken from data obtained by Hallock (1952).

[b] These levels of available P (soluble in 0.002 N H_2SO_4) and available K (exchangeable) except lowest which are natural were established in 1944 by applying superphosphate and muriate of potash, respectively; have since received some additional phosphate and also some manure.

[c] These pH levels are the result of applying finely ground dolomitic limestone in 1944.

applied phosphates. For the 1948 season, due possibly because of lack of moisture and resulting low yield of first cutting, the results were not so striking, although the trend was still the same. All in all, these results support the contention that liming of acid soils favors the availability of native and applied phosphates. Many of the data in the literature pertaining to this phase of the subject are rather confusing, because insufficient lime to bring the pH up to 7 or thereabouts was probably used in many of the experiments from which the data were derived.

III. Laboratory Tests

Over 50 years ago, Dehérain (1892) described an experiment which he said showed that treatment of an iron phosphate with calcium carbonate will cause a transformation such that some of the phosphate will become soluble in carbonated water and thus available for crop use. In more recent years, alkaline solutions, usually of NaOH and Na_2CO_3, have been used to extract the so-called fixed or difficultly available phosphorus of soils.

Because the liming of acid soils to near pH 7 appears to make difficultly available soil phosphorus soluble in weak acid rather rapidly, the

writer with the assistance of J. L. Dionne conducted a simple test to demonstrate this matter. To samples of two strongly acid soils various amounts of $CaCO_3$ were added. One series of samples of each soil was then stored in moist condition for 110 days, a second series was boiled with water for 10 minutes, and a third series was digested with water on the hot plate for 24 hours. Samples in each case were then extracted with 0.002 *N* H_2SO_4 in the regular manner for readily available phosphorus. The results are given in Table IV.

TABLE IV

PHOSPHORUS SOLUBLE IN WEAK ACID IN SPENCER SILT LOAM AND PLAINFIELD SAND

		Pounds per acre P soluble in 0.002 N H_2SO_4 after treatments given below		
			2 g. of soil treated with respective amounts of $CaCO_3$ and 50 ml. of water	
Tons per acre $CaCO_3$ added[a]	*pH after 110 days*	*Moist soil incubated for 110 days*	*Boiled for 10 minutes*	*Digested on hot plate for 24 hours with condenser*
		Spencer silt loam		
None	4.6	33.2	28.3	28.3
2	6.2	33.2	35.5	42.8
3	6.4	37.0	42.1	50.6
5	6.7	50.8	50.0	62.5
10	...	....	49.8	63.3
		Plainfield sand		
None	4.6	54.5	49.0	57.0
1.4	5.5	57.5	72.9	85.1
2.5	6.5	85.0	86.1	100.7
4.0	7.4	93.0	102.3	119.3
10.0	...	...	108.4	133.5

[a] Lime requirements by Patel-Truog (1952) method was 5 tons for Spencer silt loam and 3 tons for Plainfield sand.

It will be noted that application of lime, particularly to near the neutral point, has markedly increased the amount of phosphorus dissolved in each case. Boiling of the lime-treated samples with water for 10 minutes gave nearly the same results as storage in moist condition for 110 days. Also, the sharpest increase in easily soluble phosphorus appears to take place near the neutral point. This simple experiment demonstrates that the liming of distinctly acid soils up to near pH 7 or above will rather rapidly transform considerable amounts of difficultly available phosphorus to a readily available form. Barbier and Chabannes (1949) conducted a somewhat similar experiment and obtained similar results.

IV. Chemistry Involved

1. Early Ideas

Voelcker (1863) treated a number of soils with a soluble phosphate and noted a rapid absorption from solution of the phosphate. He concluded that the phosphate was removed from solution by lime and the hydrates of iron and aluminum. He indicated that phosphate thus absorbed is quite available to crops, and made no attempt to differentiate availabilities based on nature of absorbent. He was one of the first, if not the first, to suggest absorption of soluble fertilizer phosphate by the hydrated iron and aluminum oxides of soils.

Dehérain (1892) cites the case of a soil exceptionally rich in iron oxide which responded markedly to annual applications of phosphate fertilizer; however, after a heavy dose of marl, good yields were obtained without further phosphating.

Hilgard (1907) states that high percentages of finely divided ferric hydrate in soils may, especially in the absence of lime carbonate, render even large supplies of phosphoric acid inert and useless by formation of the totally insoluble ferric phosphate, and that aluminic hydrate probably acts in a similar manner. He cites examples of Hawaiian soils which, although having an exceedingly high content of phosphoric acid, nevertheless, because of their high content of ferric oxide, respond decidedly to phosphate fertilizer. These soils are also relatively low in acid-soluble calcium.

2. Recent Ideas

During the past twenty-five years, an extensive literature has developed with respect to the substances and reactions which are involved when soils absorb and take out of solution soluble phosphates added as fertilizer. A select list of references in this connection has recently been compiled by Wild (1950) and Black and Pierre (1951). On the basis of the evidence obtained over this period, it appears that hydrated iron oxide, probably usually goethite (FeOOH), is the principal substance in most acid soils which combines with soluble phosphate in such a manner that the phosphate is made insoluble or only very slightly soluble in weak acids, such as carbonic and 0.002 *N* H_2SO_4. Hydrated aluminum oxide can act in a similar manner, but the phosphate probably does not become nearly so difficultly available. Kaolinite and clays of the montmorillonite type also absorb soluble phosphates, but the exact forms of the combinations have not as yet been definitely revealed. Tests made in the author's laboratory indicate that the phosphate absorbed by the latter clays is rather easily extracted with water and weak

acids, and is thus probably for the most part readily available for crop use. Details regarding the manner of combination and substances formed are found in other chapters. The information here will deal briefly with some of the chemistry involved when soluble phosphates are absorbed by soils and released through the action of lime or otherwise. This discussion will be limited to absorption by, and release from, goethite and the *montmorillonite* type of clay.



FIG. 1. Growth of corn in quartz cultures with different phosphates (Truog, 1918). The tricalcium, aluminum, and iron phosphates (nonbasic) were precipitated from solution, dried at 100° C, and mixed in the quartz. All other nutrients than phosphate were supplied in water-soluble forms. (86–Check, no phosphate. 89–Superphosphate. 92–Rock phosphate. 95–Tricalcium phosphate. 98–Aluminum phosphate. 101–Ferro phosphate. 104–Ferric phosphate.)

A possible reaction that may take place when goethite absorbs soluble phosphate under acid conditions is the following:

$$Fe(=O)(OH) + H_3PO_4 = Fe(=O)(H_2PO_4) + H_2O$$

The release through liming may be represented as follows:

$$2Fe(=O)(H_2PO_4) + 2Ca(OH)_2 = 2Fe(=O)(OH) + Ca_2H_2(PO_4)_2 + 2H_2O$$

The $Ca_2H_2(PO_4)_2$ may, under the influence of an excess of $Ca(OH)_2$, go to $Ca_3(PO_4)_2$. However, under either condition the phosphate will be soluble in carbonated water or other weak acid, and thus be readily available for crop use.

As shown in Fig. 1 (Truog, 1918), corn can feed rather well on precipitated tricalcium phosphate and also on aluminum phosphate.

However, the aluminum phosphate ($AlPO_4$) used here undoubtedly had a much higher availability than the basic type formed in soils.

Because the crystalline form of the iron phosphate formed when goethite is digested with an excess of soluble phosphate corresponds on analysis to $FePO_4 \cdot 2H_2O$, some prefer the formula $Fe(OH)_2H_2PO_4$ rather than $FeOH_2PO_4$. To satisfy this condition, the latter may be written as $FeOH_2PO_4 \cdot H_2O$. Because of the ease with which $Fe\begin{matrix}O\\ \diagup\\ \diagdown\\ OH\end{matrix}$ absorbs phosphate and releases it again to OH ions, the writer does not favor the formula $Fe(OH)_2H_2PO_4$, which necessitates the more difficult displacement of double-bonded O.

Absorption by and release of phosphate from the montmorillonite type of clays may be represented as follows:

$$\text{Clay} = \text{Ca} + H_3PO_4 = \text{Clay}\begin{matrix}H\\ \diagup\\ \diagdown\\ Ca\end{matrix} H_2PO_4$$

The phosphate thus fixed is easily extracted with carbonated water or other weak acid and is thus readily available for crop use:

$$\text{Clay}\begin{matrix}H\\ \diagup\\ \diagdown\\ Ca\end{matrix} H_2PO_4 + 2H_2CO_3 = \text{Clay}\begin{matrix}H\\ \diagup\\ \diagdown\\ H\end{matrix} + Ca(HCO_3)_2 + H_3PO_4$$

High base saturation of soils through liming will favor this type of phosphate absorption and thus high availability of soil phosphorus. Barbier and Chabannes (1949) give evidence favoring this type of phosphate absorption when base saturation with calcium is high.

V. The Phosphorus Cycle

It is of interest to note that phosphorus in its cycle from rocks to soils to plants to animals and back to rocks again is associated with calcium to a large extent throughout. This cycle is illustrated schematically in Fig. 2. It is usually assumed that in igneous rocks all of the phosphorus is associated with calcium in the form of apatite. In animals, also, phosphorus is associated largely with calcium. Information in this connection provided by Sherman (1947) is as follows: About 90 per cent of the phosphorus and over 99 per cent of the calcium of the human body occur in the skeleton; here the Ca:P ratio by weight is about 2:1, and the mineral portion of bone approximates the formula

$CaCO_3 \cdot 3Ca_3(PO_4)_2$ in which Fe, $(OH)_2$, SO_4, and O may substitute for the CO_3 radical. Calcium and phosphorus are by far the most abundant mineral elements in the human body, making up about 2 and 1 per cent, respectively, of its total weight.

In soils, phosphorus is associated with calcium to varying degrees, depending upon the soil pH and supply of calcium. When soils are

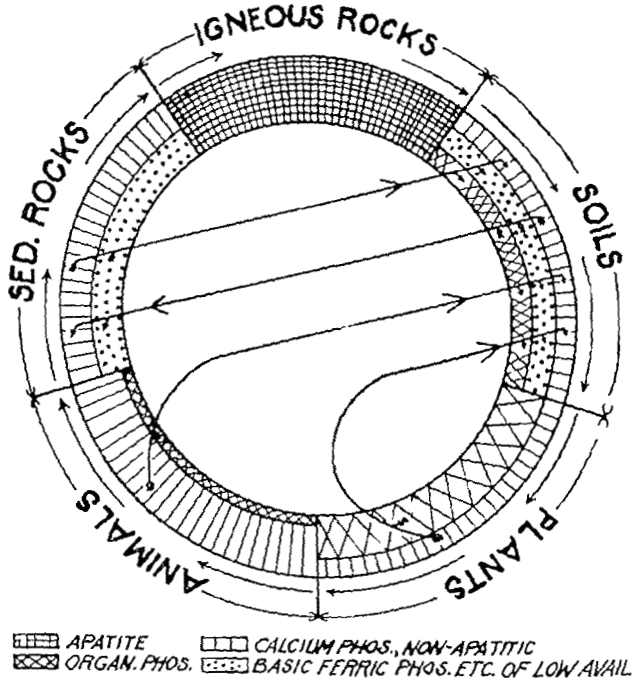


FIG. 2. The phosphorus cycle, showing relative proportions by width of bands of main forms of phosphorus that may exist at various stages, starting with the apatite of igneous rocks and going successively to various forms in soils, plants, animals, and sedimentary rocks. As indicated by internal arrows, phosphorus of plants and animals may return directly to soils. Also soils and sedimentary rocks including their phosphorus may revert directly from either to the other. Association of phosphorus with calcium throughout the cycle is brought into strong focus.

highly calcareous (contain 5 per cent or more of $CaCO_3$), most of the phosphorus is usually associated with calcium in the form of calcium phosphate which may be more or less apatitic. Under these conditions, a low level of available phosphorus for crop use often exists. When the pH of soils is near the neutral point, 10 to 25 per cent of the phosphorus they contain often exist as calcium phosphate (non-apatitic). This is a very satisfactory state, because under these conditions crops will be able to obtain an ample supply of phosphorus for good growth, provided,

of course, that the pH has been at that level for some time, and that the total supply of phosphorus in the soil is at a satisfactory level. When the pH of soils drops below 6.5, the tendency for phosphorus to be associated with calcium drops rapidly, as does usually also the availability of the phosphorus for crop use. In Fig. 2, the phosphorus of the soil is distributed about evenly between the three general forms—organic, iron and other mineral phosphates of low availability, and calcium phosphate. This distribution represents a satisfactory condition as regards a favorable supply of available phosphorus for crop needs.

In plants, the proportion of various forms of phosphorus in the seeds is quite different from what it is in the vegetative organs: in the former, only 10 per cent may be mineral, and of the 90 per cent which may be organic, 50 per cent and often much more may exist in phytin; in the vegetative organs, 50 per cent or even more of the phosphorus is usually in mineral form, and this, presumably, often quite largely as calcium phosphate. Analyses by Mather (1929) show that the total phosphorus content of a forage like alfalfa may be increased from about 0.15 per cent to about 0.40 per cent and even more by increasing the supply of available phosphorus in the soil on which the alfalfa is grown; also, this increase arises largely from an increase in the mineral portion rather than from a marked increase in the organic portion; the mineral portion may go from less than 50 to over 60 per cent of the total. This is highly important from an animal nutrition standpoint, because recent publications by Corrie (1948), and Linton and Williamson (1934) raise a moot question with regard to the availability of phytin phosphorus for nutrition, particularly, of chickens. The manure analyses of Peperzak (1948) are enlightening in this connection. They show a very low content of phytin phosphorus in the fresh excrement of farm animals except chickens, where it may represent 10 to 15 per cent of the total. This indicates, in general, a satisfactory availability of phytin phosphorus in animal nutrition. Be this as it may, there appears to be no question but that the mineral phosphates of plants are highly available in animal nutrition. Thus, the liming of acid soils assumes great importance, not only in promoting a favorable supply of available phosphorus for crops, but likewise for animals.

The critical stage in the phosphorus cycle is the soil stage, because the availability of the phosphorus here determines the phosphorus content of plant products on which animals feed. It is well known that these products are often too low in phosphorus content to meet satisfactory nutritional standards, making it necessary to make additions of mineral phosphates to animal feeds. On the basis of data now available, it appears safe to say that these additions could be largely eliminated

through adequate liming of the acid soils on which the feeds are grown, particularly, the legume forages.

VI. Discussion

There appears to be no question but that the liming of acid soils to a pH near the neutral point will promote the availability both of native soil phosphorus and of that applied as a soluble fertilizer. The case of rock phosphate, however, in this connection presents a dilemma: For the availability of rock phosphate to be at all satisfactory, soils must be kept distinctly acid, that is, at pH 6.0 or lower; unfortunately, in this pH range, the phosphorus of rock phosphate on becoming soluble and available is, when not absorbed shortly by a crop, usually fixed by iron oxide in difficultly available form. Thus, gradually the phosphorus of rock phosphate changes to an even less available form. On the other hand, if the soil is limed to near the neutral point, the solubility of the rock phosphate itself will be far too low to give satisfactory results.

There exists abundant evidence that the liming of acid soils to near or above the neutral point will make some of the minor nutrient elements less soluble and available (Truog, 1946). If the total supply in a soil of one or more of these elements is low, it may become necessary to make suitable additions. This, however, should not induce a farmer to forego the tremendous benefits derived from liming acid soils to near the neutral point, because these benefits will usually far outweigh the cost of adding the minor elements. Moreover, this liming by reducing the solubility of the minor elements will tend to reduce their loss by leaching. The high solubility of most of the minor nutrient elements under acid conditions means also that these elements will be lost more rapidly by leaching. This loss is one reason why acid soils are often low in their total supply of some of the minor elements, particularly boron.

Liming of acid soils to near pH 7 and addition of such minor elements as may be needed is usually the best method of building a soil to its highest state of general fertility. This will make possible the addition of active organic matter, particularly, through the growing of luxuriant crops of alfalfa, clover, and other legumes; in time, this organic matter will eliminate all minor element difficulties that may be experienced by liming up to pH 7 or thereabouts, which is necessary if a soil is to be brought to its highest state of fertility for all but a few special crops that do best under distinctly acid conditions.

During the past 100 years or more, the liming of acid soils has received vigorous reoccurring attention by a number of investigators and writers. Johnston (1849) and Ruffin (1852) were among the first to

write extensively and authentically on the subject, but had no way of knowing about the favorable influence of liming on phosphorus availability. Following this, during the last half of the nineteenth century, more and more attention was given to fertilizers and relatively less to lime. Near the close of the nineteenth century Wheeler (1897) summarized his extensive investigations dealing with the liming of acid upland soils, and called attention to the favorable influence of this practice on phosphorus availability; his researches and writings did much to revive interest in the liming of soils in this country. Also, a little later, Whitson and Stoddart (1906) suggested that a distinctly acid condition of a soil is practically a certain indication that the soil is lacking in available phosphorus. However, partly because of the rapidly growing interest in and need of fertilizers and the striking results which they produced, the great importance of liming was kept somewhat in the background. Thus, even today, there is no question but that a revival of emphasis in adequate liming is needed. Because of the great benefits produced by liming, especially with respect to phosphate availability, and the knowledge we now have as regards the mode of action of lime including influence on availability of minor elements, it would appear that the time has arrived when most acid soils devoted to general farming should be limed to near pH 7.

In the early use of lime, very heavy doses of quicklime were sometimes applied. Such use often gave large increases in crop yields at first, but in time the yields declined sharply, giving rise to the proverb:

> "Lime and lime without manure,
> Makes both farm and farmer poor."

In the light of present-day knowledge, the occurrence of such a decline in productivity may be explained as arising most often from an exhaustion of the supply of available potassium. The results reported by Salter and Barnes (1935) show that when potassium and nitrogen were applied with the lime, there was an increase rather than a decrease in productivity over a 40-year period. There should of course be no question about the effects of liming: calcium and magnesium are thereby added and soil conditions in general are improved so that the resulting higher yields, particularly of legumes, will necessarily cause a heavier drain on the supply of available potassium and other elements. Regardless of the system of soil management, it must be expected that the larger the crop yields, the greater will be the drain on fertility elements, and the greater will be the need of their replenishment in time. Liming helps to provide the conditions that make possible the most effective and economical use of the fertility elements naturally present

in soils and supplied in manure and fertilizers, and the foregoing proverb could well be reversed to read as follows:

"Manure and fertilizer without lime,
Will ruin both farm and farmer in time."

To meet the rapidly increasing need for greater food supplies and the ever rising labor costs, the pressure increases constantly to attain maximum yields. This means that for general farm crops, soils will need to be limed to near the neutral point in order that the soil phosphate and that applied as fertilizer may retain a high state of availability. For maximum yields of a rapidly growing and potentially very high-yielding crop like corn, some locally applied fertilizer will always be needed even though a high state of fertility including a reaction of approximately pH 7 is being maintained; however, under these conditions, the amount needed of the locally applied phosphate will be less.

References

Barbier, G., and Chabannes, J. 1949. Sur le méchanisme de l'adsorption des phosphates par divers constituants des argiles des sols. *Ann. Agron.* **19**: 343–379.

Black, C. A., and Pierre, W. H. 1951. Phosphate fertilizers. *In* Agricultural Chemistry, Vol. II, Applications, pp. 248–276. Donald E. H. Frear, Editor. D. Van Nostrand Co., New York.

Corrie, F. E. 1948. Some Elements of Plants and Animals. Fertiliser Journal Ltd., London.

Dehérain, P. P. 1892. Traité de chimie agricole. Libraire de L'Academie de Médecine, Paris.

Hallock, D. L. 1952. Relation of forms and amounts of soil phosphorus to phosphorus content of alfalfa. Ph.D. thesis, University of Wisconsin, Madison, Wis.

Hilgard, E. W. 1907. Soils, Their Formation, Properties, Composition, and Relations to Climate and Plant Growth in the Humid and Arid Regions. The Macmillan Company, New York.

Johnston, J. F. W. 1849. The Use of Lime. William Blackwood and Sons, Edinburgh and London.

Liebig, J. 1847. Chemistry in Its Application to Agriculture and Physiology. 4th Ed. American reprinting 1872. John Wiley, New York.

Linton, R. G., and Williamson, G. 1943. Animal Nutrition and Veterinary Dietetics, pp. 56–59. W. Green, Edinburgh.

Mather, T. H. 1929. The effect of fertilizers upon the forms of phosphorus and the amounts of phosphorus, nitrogen, and silica in hays. *Sci. Agr.* **10**: 35–63.

Patel, D. K., and Truog, E. 1952. Lime requirement determination of soils. *Soil Sci. Soc. Amer. Proc.* **16**: 41–44.

Peperzak, P. 1948. Phosphorus compounds in manures. M.S. thesis, Iowa State College, Ames, Iowa.

Ruffin, E. 1852. An Essay on Calcareous Manures. J. W. Randolph, Richmond, Va.

Salter, R. M., and Barnes, E. E., 1935. The efficiency of soil and fertilizer phosphorus as affected by soil reaction. *Ohio Agr. Expt. Sta. Bull.* **553**.

SHERMAN, H. G. 1947. Calcium and Phosphorus in Foods and Nutrition. Columbia University Press, New York.

TRUOG, E. 1918. The utilization of phosphates by agricultural crops, including a new theory regarding the feeding power of plants. *Wisconsin Agr. Expt. Sta. Research Bull.* 41.

TRUOG, E. 1946. Soil reaction influence on availability of plant nutrients. *Soil Sci. Soc. Amer. Proc.* 11: 305–308.

VOELCKER, A. 1863. III. On the absorption of soluble phosphate of lime by different soils of known composition, and remarks on the application of superphosphate and other phosphatic manures to root crops. *J. Royal Agr. Soc.* 24: 37–65.

WHEELER, H. J. 1897. Lime and liming. *Rhode Island Agr. Expt. Sta. Bull.* 46.

WHITSON, A. R., and STODDART, C. W. 1906. Availability of phosphates in relation to soil acidity. *Wisconsin Agr. Expt. Sta. Ann. Rept.* 1906: 171–180.

WILD, A. 1950. The retention of phosphates by soil. A review. *J. Soil Sci.* 1, No. 2: 221–238.



CHAPTER X

Laboratory Evaluation of Phosphate Fertilizers

K. D. JACOB and W. L. HILL

I. Introduction

Chemical control methods have been necessary from the beginning of the phosphate fertilizer industry. Proper factory operation early demanded a modicum of chemical control that would insure a reasonably uniform product with economical use of raw materials. Before long, market competition and consumer protection required the development of tests for quality of products from different sources. Since the primary object of the industry is the conversion of slightly soluble natural phosphates, now mainly phosphate rock, into more soluble phosphates, solubility constituted a logical criterion of quality. In fertilizer usage *solubility* refers to the amount of phosphorus that can be leached or extracted from a sample under stated conditions rather than to the thermodynamic solubility. Indeed, many fertilizer materials do not possess a true solubility. In its fertilizer connotation quality also refers to the efficacy of the phosphate material as a nutrient for growing vegetation, and hence, the ultimate test of its quality is its performance in the field. Accordingly, much labor has been expended in efforts to develop procedures for rapid chemical tests that may be expected to place sundry phosphate fertilizers in the same order with respect to quality as would be obtained in field testing. The two general types of tests give two measures of quality: the one being a result of a laboratory determination based on solubility, called *available phosphorus* in North America, which has been written into the statutes of many jurisdictions both at home and abroad; the other being a composite of crop-response tests under a variety of conditions, which is called nutrient value, vegetative availability (the parallel term being chemical availability), or fertilizer efficiency.

In North American fertilizer parlance, phosphates are divided into three categories (water-soluble, citrate-soluble, and citrate-insoluble) that represent roughly defined ranges of solubility. For example, the point of division between water-soluble and water-insoluble phosphates

lies somewhere between the solubility of monocalcium phosphate, which is classed as water-soluble despite its decomposition in contact with water to form dicalcium phosphate, and dicalcium phosphate, which is classed as water-insoluble despite the fact that its thermodynamic solubility is just under 2 millimoles of PO_4 per liter. However, the haziness of the borderline has not caused confusion, because the wide gap between the solubilities of known phosphate compounds in the two broad groups leaves little chance for doubt. Similarly, the water-insoluble phosphates are divided into two groups on the basis of their solubilities in specially prepared solutions containing citrate ion. The specifications for the reagent vary from country to country, and use is made of both neutral and alkaline ammonium citrate solutions, as well as solutions of citric acid, so that the nature of the solution must be stated or understood in discussions. In this country, where neutral ammonium citrate is the accepted reagent, citrate solubility without qualification refers to the neutral reagent. As a consequence of the separation of water-insoluble phosphates into two categories, the solubility of many crystalline phosphate compounds can be referred to either of two solubility scales. A little logic and considerable discretion permit the alignment of the scales shown in Fig. 1, for among the calcium phosphates dicalcium phosphate is considered completely soluble in neutral citrate solution, whereas fluorapatite is nearly insoluble. Thus, it would appear that the determination of the citrate solubility of a phosphate compound is a quick method for estimating the order of its water solubility. Accordingly, 50 per cent citrate solubility would correspond with a water solubility of the same order as that of silver chloride at 25° C., which is one of the least soluble compounds used in gravimetric chemical analysis. Whereas the water-soluble phosphate compounds lie in the thermodynamic solubility range, 1 to 10 moles of PO_4 per liter, the water-insoluble calcium phosphates that are more or less soluble in neutral citrate solution are spread over a range from 10^{-3} down to 10^{-7} mole of PO_4 per liter. As a convenience in classifying the water-insoluble citrate-soluble compounds, subdivision of the range is desirable. To this end a citrate solubility below 30 per cent is considered *low*, 30 to 70 per cent *medium*, and above 70 per cent *high*.

The attempt to make solubility by one procedure or another parallel the nutrient value shown by crop response, also measured by sundry methods under widely variable conditions, has resulted in the development in fertilizer-consuming countries of procedures for solubility determination that have been accepted as official methods for the rapid evaluation of the quality of fertilizer offered to the farmer. Considerable variation is to be expected in laboratory procedures developed

under different conditions as regards the marketed fertilizer materials and their use. Among other qualifications, the method should reflect, first of all, the approximate nutrient value of the phosphorus in the condition as marketed and applied to the soil, with respect to a wide variety of crops under different circumstances of soil, climate, and

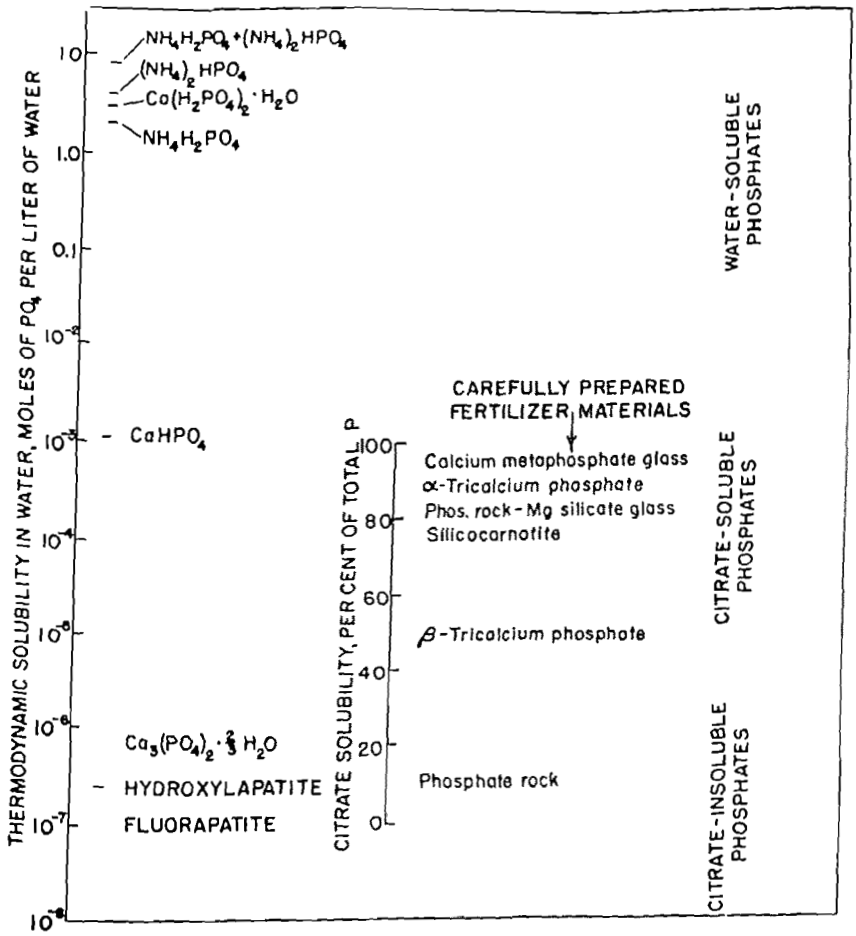


FIG. 1. Scales of solubility for ammonium and calcium phosphates. (Hill, 1951.)

farming practices. It should be applicable to different types of fertilizer materials and mixtures. It should be capable of rapid execution, and it should yield precise results in the hands of different analysts.

The purpose of this chapter is to bring together descriptions of the several methods, classified as far as possible for ready comparison, and to give a brief account of the experimental bases on which their merits

rest. A proper perspective of the methods, however, requires a full appreciation of the wide variety of materials under test.

II. Phosphate Fertilizer Materials

Phosphate-containing fertilizers may differ by virtue of (1) type of phosphorus compound, (2) assemblage of phosphorus compounds, (3) degree of crystallinity, (4) fineness, (5) associated nonphosphate compounds, and (6) the disposition of the compounds with respect to one another. As a matter of convenience, the second and third dimensions of variability are combined in the following discussion, as also are the fifth and sixth.

1. Phosphate Compounds Found in Fertilizers

A number of phosphate compounds that are met in fertilizers and related materials are listed in Table I. This list, far from being an exhaustive one, consists of 41 compounds, inclusive of amorphous and crystalline modifications, and is composed of 23 orthophosphates, 7 pyrophosphates, 7 metaphosphates, and 4 polyphosphates. Only 10 of them are water-soluble in the fertilizer sense, and 2 of these, being hygroscopic thermal products with a low calcium to phosphorus ratio, are unsuited for fertilizers; the remaining compounds exhibit a wide range of citrate solubility. The prominence of calcium salts among fertilizer phosphates is witnessed by the observation that 31 of the listed compounds contain this element. The bulk of the phosphorus in domestic processed fertilizers is carried in three compounds—monocalcium phosphate monohydrate, anhydrous dicalcium phosphate, and monoammonium phosphate. Smaller but important amounts are carried in phosphoric acid, calcium metaphosphate glass, and alpha tricalcium phosphate. Considerable amounts also occur as poorly defined forms that often contain fluorine, such as the basic phosphates (inclusive of hydrated tricalcium phosphate) in ammoniated superphosphate and mixtures containing it and calcium iron (aluminum) phosphates in superphosphate and fertilizer-grade ammonium phosphate.

2. Degree of Crystallinity

In contrast with the homogenous compounds in pure form discussed above the most common phosphate fertilizers are assemblages of two or more phosphate-containing entities. For example, fertilizer-grade monoammonium phosphate is a mixture of monoammonium phosphate and a poorly defined and in part amorphous substance derived from impurities in the phosphoric acid; dicalcium phosphate is likely to be a mixture of the anhydrous and hydrated compounds; furnace products

TABLE I

PHOSPHATE COMPOUNDS OCCURRING IN COMMERCIAL OR EXPERIMENTAL FERTILIZERS[a]

Item	Name or type	Formula	Range of thermal stability,[b] °C.	Citrate solubility[c]	Occurrence[d]
	Orthophosphates				
1	Phosphoric acid, aqueous[e]	H_3PO_4		High (w)	Fertilizer material, superphosphate
2	Ammonium phosphate, primary[e]	$NH_4H_2PO_4$		High (w)	Fertilizer material, am. superphosphate
3	secondary	$(NH_4)_2HPO_4$		High (w)	Fertilizer material, hv. am. triple superphosphate
4	Potassium phosphate, primary	KH_2PO_4	− 190	High (w)	Special preparation
5	Magnesium ammonium phosphate	$MgNH_4PO_4 \cdot 6H_2O$ or H_2O		High	Mixtures of dolomite and am. superphosphate
	Calcium phosphate:				
6	Primary, monohydrate[e]	$Ca(H_2PO_4)_2 \cdot H_2O$	− 100	High (w)	Superphosphate
7	anhydrous	$Ca(H_2PO_4)_2$	− 150	High (w)	Superphosphate
8	Secondary, dihydrate	$CaHPO_4 \cdot 2H_2O$	− 25	High	Am. superphosphate
9	anhydrous[e]	$CaHPO_4$	− 200	High	Am. superphosphate
10	Tertiary, hydrate[f]	$Ca_3(PO_4)_2 \cdot 2/3H_2O$	− 600	Low	Hv. am. superphosphate[g]
11	anhydrous	β-$Ca_3(PO_4)_2$	−1115 t	Medium	Thermally defluorinated phosphate
12	anhydrous[h]	α-$Ca_3(PO_4)_2$	1115 to m	High	Defluorinated phosphate rock
13	Tetracalcium phosphate	$Ca_4P_2O_9$	Decomposed by H_2O	High	Basic slag
14	Silicocarnotite	$Ca_3(PO_4)_2 \cdot Ca_2SiO_4$	−1850 m	High	Basic slag, Rhenania phosphate[i]
15	Nagelschmidtite	$Ca_3(PO_4)_2 \cdot 2Ca_2SiO_4$	−m	High	Basic slag
16	Calcium sodium phosphate[j]	$CaNaPO_4$	+ 680 t	High	Rhenania phosphate
17	Apatite[e]	$Ca_{10}(PO_4)_6(OH,F)_2$	−1350	Low	Phosphate rock
18	Pseudowavellite	$5CaO \cdot 6Al_2O_3 \cdot 4P_2O_5 \cdot 18H_2O$	− 200	Low	Phosphate rock
19	Calcium iron (aluminum) phosphate[e]	$Ca[H_2Fe(PO_4)_2]_2 \cdot 6H_2O$	− 100	High	Superphosphate, ammonium phosphate
20	Aluminum phosphate, crystalline	$AlPO_4 \cdot 3H_2O$	− 100	Low	Mineral, special preparation
21	amorphous	$AlPO_4 \cdot 3H_2O$ or $AlPO_4$		High	Special preparation
22	Ferric phosphate, crystalline	$FePO_4$		Low	Special preparation
23	amorphous	$FePO_4 \cdot 3H_2O$		High	Special preparation
	Pyrophosphates				
	Calcium pyrophosphate:				
24	Acid salt, crystalline	$CaH_2P_2O_7$	− 280	High (w)	Special preparation
25	amorphous	Variable composition	200 to 600	High (w)	Heated superphosphate
26	Normal salt, amorphous	$Ca_2P_2O_7 \cdot 4H_2O$		Medium	Special preparation
27	dihydrate	$Ca_2P_2O_7 \cdot 2H_2O$	− 250	High	Special preparation
28	anhydrous	γ-$Ca_2P_2O_7$	− 700	Low	Heated superphosphate
29	anhydrous	β-$Ca_2P_2O_7$	−1140 t	Low	Heated superphosphate
30	anhydrous	α-$Ca_2P_2O_7$	1140 to 1153 m	Low	Special preparation

TABLE I (*Continued*)

Item	*Name or type*	*Formula*	*Range of thermal stability,*[b] °C.	*Citrate solubility*[c]	*Occurrence*[d]
			Metaphosphates		
31	Potassium metaphosphate	KPO_3	− 810 m	High	Special preparation
	Calcium metaphosphate:				
32	Low-temperature form	δ-$Ca(PO_3)_2$	− 600	High	Heated superphosphate
33	Low-temperature form	γ-$Ca(PO_3)_2$	− 600	High	Heated superphosphate
34	Sulfate-metaphosphate complex[j]	....	− 600	High	Heated superphosphate
35	High-temperature form	β-$Ca(PO_3)_2$	− 963 t	Low	Heated superphosphate
36	High-temperature form	α-$Ca(PO_3)_2$	963 to 984	Low	Special preparation
37	Amorphous form[e]	Glass	+ 984 m	High	Fertilizer material
			Polyphosphates		
38	Trömelite	$7CaO{\cdot}5P_2O_5$	915 t to 985 m	Low	Special preparation
39	Calcium hexaphosphate	$Ca_2P_6O_{17}$	− 774 m	High (w)	Special preparation
40	Calcium tetraphosphate	CaP_4O_{11}	− 810 m	High (w)	Special preparation
41	Calcium triphosphate	$Ca_2HP_3O_{10}$	− 550	High	Heated superphosphate

[a] List compiled by Hill (1947) with the addition of items 1 to 5, 19 to 23, and 31, inclusive.

[b] Melting points are indicated by the letter m, and transition points by t; other temperatures are approximate.

[c] In neutral citrate solution. Water solubility is indicated by (w). Degree of citrate solubility is designated thus: *high* above 70%, *medium* 30 to 70%, and *low* below 30% of the total phosphorus.

[d] Superphosphate unaccompanied by the modifiers "normal" or "triple" embraces both. Lightly and heavily ammoniated superphosphate, respectively, is indicated by am. and hv. am. superphosphate.

[e] Compound commonly met in domestic fertilizers.

[f] An apatite-like compound of variable composition; the composition corresponding with the formula is apparently one of a continuous series reaching from a CaO to P_2O_5 mole ratio somewhat less than 3 to that for hydroxylapatite (Eisenberger *et al.*, 1940). The formula without its water component is frequently used in chemical equations as a convenience in balancing materials, but this practice is not to be regarded as evidence for the existence in fertilizers of a compound having this particular composition.

[g] The tricalcium phosphate in heavily ammoniated superphosphate is amorphous in part.

[h] In Rhenania phosphate the silicocarnotite is a sodium-bearing variety.

[i] The solubility of the low-temperature form stable below 680° C. has not been determined.

[j] Contains about 2 moles of calcium sulfate per mole of calcium metaphosphate.

often carry an amorphous phase as well as crystalline compounds; and superphosphate usually contains besides monocalcium phosphate monohydrate a small amount of unreacted rock and more or less amorphous material in both solid and liquid forms. The gel-like nature of superphosphate is discussed by Lehrecke (1935). Thus, phosphate materials are subject to wide variations in composition and behavior as a consequence of differences both in the phase assemblages and in the degree of crystallinity. The more common cases are covered in the following classification:

A. CRYSTALLINE PHOSPHATE COMPOUNDS.
   1. *Single homogeneous compound.* An example is monoammonium phosphate made from electrothermal acid.
   2. *Two or more compounds.* An example is a mixture of monoammonium and diammonium phosphates made from electrothermal acid.

B. AMORPHOUS PHOSPHATE COMPONENTS.
   1. *Single homogeneous phase.* Calcium metaphosphate glass and also glass obtained by fusing phosphate rock and magnesium silicate.
   2. *Two or more phases.* Phosphate rock–magnesium silicate glass often contains identifiable amounts of glass with an index of refraction, and hence a chemical composition, appreciably different from that of the main body of material.

C. BOTH CRYSTALLINE AND AMORPHOUS COMPONENTS.
   1. *Phases have same chemical composition.* A partially fused compound that melts congruently, for example, calcium metaphosphate. The amorphous phase has the higher solubility.
   2. *Phases have different chemical compositions.*
      a. One amorphous, one crystalline. Fused tricalcium phosphate consists of a phosphate-containing glass and alpha tricalcium phosphate. In some samples, at least, the glass has the lower citrate solubility.
      b. One amorphous phase or more and two or more crystalline phases. Ammonium phosphate made from wet-process acid, which consists of monoammonium phosphate and a complex component containing phosphorus, aluminum, iron, fluorine, etc., that is in part amorphous; fairly fresh superphosphate, which is composed of monocalcium phosphate, unreacted rock, liquid solution, and some amorphous solid phosphate substance; and ammoniated superphosphate consisting of monoammonium phosphate, dicalcium phosphate, and more or less amorphous solid phosphate substance.

Perhaps the chief value of this exercise in classification with examples lies in the emphasis it gives to the great complexity of the most widely used domestic phosphate fertilizer materials. The more common ones fall in the last group. In general, the number of dimensions of variability is large, and consequently the solubility determinations required by practical tests of fertilizer quality cannot be expected to yield reliable information on the specific behavior of any single component. Nevertheless, the result has significance as an index of the behavior of the assemblage and therewith the quality of the phosphate contained

TABLE II

SOLUBILITY OF SOME PHOSPHATE-CONTAINING FERTILIZERS

Material	Fineness of sample, mesh	Total P_2O_5, per cent	Percentage of total P_2O_5		
			Water-soluble	Citrate-soluble[a]	Available
Ammonium phosphate, 11–48–0	– 20	49.3	89	9	98
Ammonium phosphate,[b] 16–20–0	– 20	21.1	86	12	98
Superphosphate, normal	– 20	20.5	78	18	96
Superphosphate, triple	– 20	46.9	84	13	97
Ammoniated superphosphate[c]	– 35	19.7	54	36	90
Ammoniated superphosphate[d]	– 35	19.1	21	63	84
Dicalcium phosphate	.....	40.4	5	91	96
Byproduct phosphate[e]	– 80	39.7	4	93	97
Calcium metaphosphate glass	– 80	63.6	1	98	99
Phosphate rock–magnesium silicate glass[f]	– 80	22.1	0	88	88
Fused tricalcium phosphate	–100	28.1	0	79	79
Basic slag, domestic	–100	11.9	0	86	86
Rhenania phosphate[g]	–100	26.1	0	92	92
Florida land-pebble rock[h]	–100	33.0	0	8	8
Bonemeal	.....	24.5	0	57	57
Mixed fertilizer, 3–12–6	– 35	12.4	57	41	98
Mixed fertilizer, 5–10–5	– 35	10.4	54	44	98
Ferric phosphate,[i] air-dried precipitate	– 80	32.8	..	100	100
Same after ignition at 1000° C.	– 80	43.7	..	31	31
Aluminum phosphate,[i] air-dried precipitate	– 80	36.5	..	100	100
Same after ignition at 900° C.	– 80	54.1	..	100	100
Aluminum phosphate,[i] natural	–100	42.3	0	9	9
Same after ignition at 800° C.	–100	55.4	0	76	76

[a] Determined on water-washed sample with neutral citrate solution.
[b] Contains ammonium sulfate.
[c] Neutralizing ammonia equivalent to 1.75 per cent nitrogen.
[d] Neutralizing ammonia equivalent to 5.12 per cent nitrogen.
[e] Byproduct of sodium phosphate manufacture from wet-process phosphoric acid. Similar material is responsible for citrate-soluble phosphorus in ammonium phosphate fertilizer.
[f] Prepared by fusing a proportioned mixture of phosphate rock and magnesium silicate.
[g] Produced in Germany by calcining a proportioned mixture of phosphate rock and soda ash.
[h] Solubilities of other phosphate rocks are given in Table XI.
[i] Not on the fertilizer market.

in it. With mixed fertilizers the situation is usually much more complicated than with the materials. Solubilities of some phosphate fertilizers are given in Table II.

3. *Fineness Considerations*

a. Particle Size. The fineness of a particulate material is most simply defined in terms of the mesh of a sieve with openings barely large enough to allow 100 per cent of a representative sample to pass. Thus,

nothing can be said about the size of the particles except that they are smaller in two dimensions than the sieve opening. In both commercial and laboratory practice, however, fertilizer materials are often ground to pass a specified sieve by a margin, rather than being ground just to pass, whereupon the stated mesh is nothing more than a nominal fineness. This treatment is satisfactory for the preparation of samples for chemical analysis, even though the fineness cannot be accurately stated without additional measurement. The fineness of a material ground just to pass the sieve can be given moderate reliability by careful grinding in a plate mill.

For studies of the influence of particle size on the solubility pattern of fertilizers, better definition of fineness is obtained by the use of two sieves, the openings of which, differing in size, establish an upper and a lower limit of the size range. The sample thus prepared is a *size fraction* of the fertilizer, and the average size of the particles in it is assumed to be the arithmetical mean of the two sieve openings; its chemical composition, unlike that of material ground just to pass the sieve, may be different from that of the original fertilizer. Indeed, the component materials of many fertilizer mixtures can be separated fairly well by screening the mixture into size fractions.

Particle size of finely ground and granulated phosphates in relation to placement in the soil and rate of reaction of the fertilizer is discussed by Hill (1951). The influence of fineness on the citrate solubility of three furnace products and a phosphate rock is illustrated by the curves in Fig. 2. Results on samples ground just to pass the sieve agree very well with those on comparable size fractions in the case of fused tricalcium phosphate, the only material for which the data are adequate for reliable comparison on the steep part of the solubility curve. The general case in which the effect of particle size disappears at finenesses within the practical range of sieves is illustrated by the curve for metaphosphate glass. The low solubility of the coarsest Florida land-pebble phosphate was doubled by grinding it to pass the 200-mesh sieve.

b. Grain Size. The two glass materials cited in Fig. 2 are composed of one phase that is practically homogeneous, which means that the particles of the respective materials are alike except for shape and size. Furthermore, the surface area is restricted to a very considerable extent to the outer (geometrical) boundary of the particles, though cracks no doubt make a significant contribution to the total surface area. Phosphate rock, on the other hand, is composed largely of more or less inhomogeneous aggregates of small grains firmly cemented together. Whereas aggregate size is expressed in terms of sieve openings, grain size is ordinarily inferred from surface area measurements. The grain

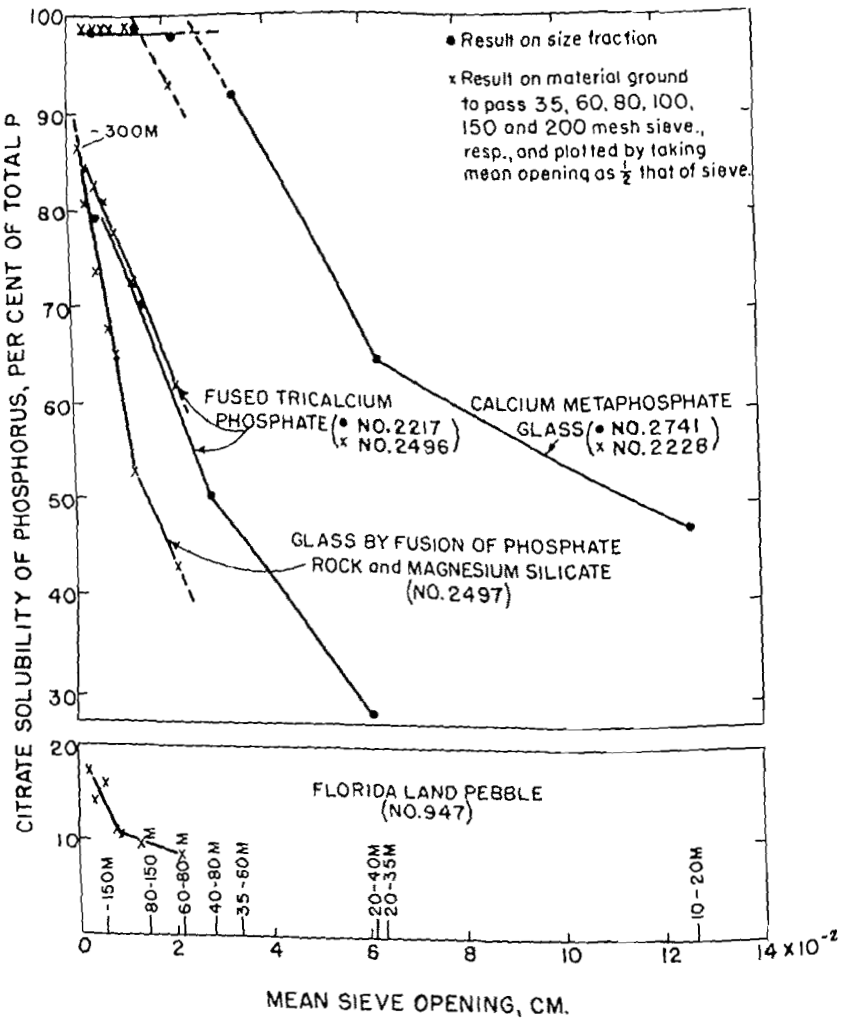


FIG. 2. Dependence of neutral citrate solubility of furnace products and phosphate rock on fineness of sample. Solubility determinations made with periodic agitation during the citrate digestion. Results on size fractions of metaphosphate glass by Jacob *et al.* (1951); those on size fractions of fused tricalcium phosphate by Armiger *et al.* (1945); others by Hill (1947).

sizes thus indicated by the measured specific surfaces of a number of phosphate materials are shown in Table III. It should be noted that the specific surface of —200-mesh phosphate rocks ranges from about 1 to 20 square meters per gram, or 20 to 400 times that for spheres having the same mean dimensions, and that for steamed bone is 66 to 67 square meters per gram, whereas the precipitated basic phosphates fall in the intermediate range. The corresponding grain sizes range from 0.03

TABLE III

AGGREGATE SIZE, SPECIFIC SURFACE, AND INFERRED GRAIN SIZE OF SOME NATURAL PHOSPHATES AND PRECIPITATED MATERIALS[a]

Item No.	*Type or source of phosphate*	*Mesh size*[b]	*Specific surface,*[c] *m^2 per gram*	*Aggregate size,*[d] *microns*	*Grain size,*[e] *microns*	*Neutral citrate solubility of phosphorus,*[f] *per cent of total*
1	Virginia apatite	−200	1.2	37	1.7	2.1
2	Curaçao Island rock	−200	5.2	37	0.39	14.0
3	Tennessee brown rock	−200	8.3	37	0.24	6.1
4	Florida land pebble	−100	11.2	75	0.18	9.3
5	Florida land pebble	−200	13.9	37	0.14	..
6	Florida land pebble	[g]	18.0	5	0.11	..
7	Morocco rock	−200	20.5	37	0.098	15.7
8	Pseudowavellite[h]	−200	20.2	37	0.099	7.9
9	Steamed bone	16–28	66.2[i]	795	0.030	.
10	Steamed bone	100–200	66.2[i]	112	0.030	
11	Steamed bone	[g]	67.0	5	0.030	...
12	Precipitated basic phosphate, $P_2O_5/CaO = 0.85$	...	63.7	..	0.031	60[i]
13	Precipitated basic phosphate, $P_2O_5/CaO = 0.79$		55.3	...	0.036	62
14	Precipitated basic phosphate, $P_2O_5/CaO = 0.80$	...	36.3	..	0.054	...
15	Precipitated basic phosphate, $P_2O_5/CaO = 0.85$	.	26.9	...	0.074	.
16	Phosphate rock–magnesium silicate glass	−150	0.1	53	20	84

[a] Unpublished data of Division of Fertilizer and Agricultural Lime, Bureau of Plant Industry, Soils, and Agricultural Engineering.

[b] Material ground just to pass sieve, unless it is indicated otherwise by footnote or by statement of upper and lower sieves. Openings of 16-, 28-, 100-, and 200-mesh sieves were 1000, 590, 149, and 74 microns, respectively.

[c] Measured by Brunauer-Emmett-Teller gas absorption method.

[d] Mean sieve opening.

[e] Diameter of nonporous sphere having same density and specific surface as phosphate. For this calculation the absolute density of the phosphates is assumed to be 3.

[f] Results for items 1 to 8 were determined on −100-mesh materials.

[g] Sample, prepared with use of Roller analyzer, was −10-micron material.

[h] Concentrate from Bartow clay, a phosphate found in Florida.

[i] Hendricks and Hill (1950).

[j] Digestion period 0.5 hour; other results 1 hour.

micron in steamed bone to 1.7 microns in Virginia apatite. The specific surface of the steamed bone (items 9 to 11) is sensibly independent of aggregate size, which indicates that the pores are all open to the outside. Although the measured surface of the Florida land pebble (items 4 to 6) increased about 63 per cent upon changing the mean aggregate

size from 75 microns to 5 microns, this increase in surface is small in comparison with the 15-fold change in aggregate dimension and can be attributed mainly to the opening of blocked pore space with reduction in particle size. Accordingly, the grain size of this rock appears to be about 0.11 micron.

In solubility studies of fertilizers the influence of grain size on solubility has not been isolated from composition effects and other factors, though surface area is often mentioned as an important factor. Interestingly enough, the neutral citrate solubility of phosphate rocks, though low, appears to parallel the measured surface areas reasonably well (Table III, last column), if allowance be made for known compositional differences, such as fluorine deficiency and a consequent preponderance of hydroxyl in Curaçao phosphate and the nonapatite nature of pseudowavellite.

c. Surface Sorption. Many of the specific surfaces listed in Table III fall within the range for colloids. In this connection the precipitated basic phosphates have a special significance, since relatively large quantities of them may be formed *in situ* in fertilizers when the superphosphate component is neutralized, wholly or in part, by the addition of ammonia or liming materials. The precipitated phosphates listed in the table, having been prepared with the hope of obtaining well-defined materials, do not cover the known range of surface areas for such materials. Basic phosphates with specific surfaces ranging from a few to nearly 150 square meters per gram can be prepared in the laboratory by suitable adjustment of the conditions of precipitation (Gee and Deitz, 1952). The sorptive character of the surface of basic phosphates is shown by the work of Lorah *et al.* (1929), Logan and Taylor (1938), and Olsen (1952), among others. Such extensive sorption surfaces developed in the presence of sorbable ions alter the true composition of the sorbent to the extent that a chemical analysis for total constituents does not reflect the true character of the initial sorbing compound. Furthermore, the crystallinity of the fine-grained sorbent is open to question, for basic phosphates, especially rapidly formed materials, are perhaps never completely crystalline initially. Nearly completely amorphous products can be prepared under practical conditions (Gee and Deitz, 1952).

The combination of small grain size, surface sorption, and degree of crystallinity, each subject to uncontrolled variation, is responsible for the poor definition of precipitated basic phosphates encountered in fertilizers. In a recent study (Hecht *et al.*, 1952) the citrate-insoluble portion of the basic phosphate in heavily ammoniated normal superphosphate was found to consist of 89 per cent crystalline apatite, 4 per

cent beta tricalcium phosphate, and 7 per cent unidentified substances. The widely variable character of laboratory preparations is illustrated by the citrate solubilities depicted in Fig. 3. Results connected by line C were obtained on preparations known to be essentially one phase

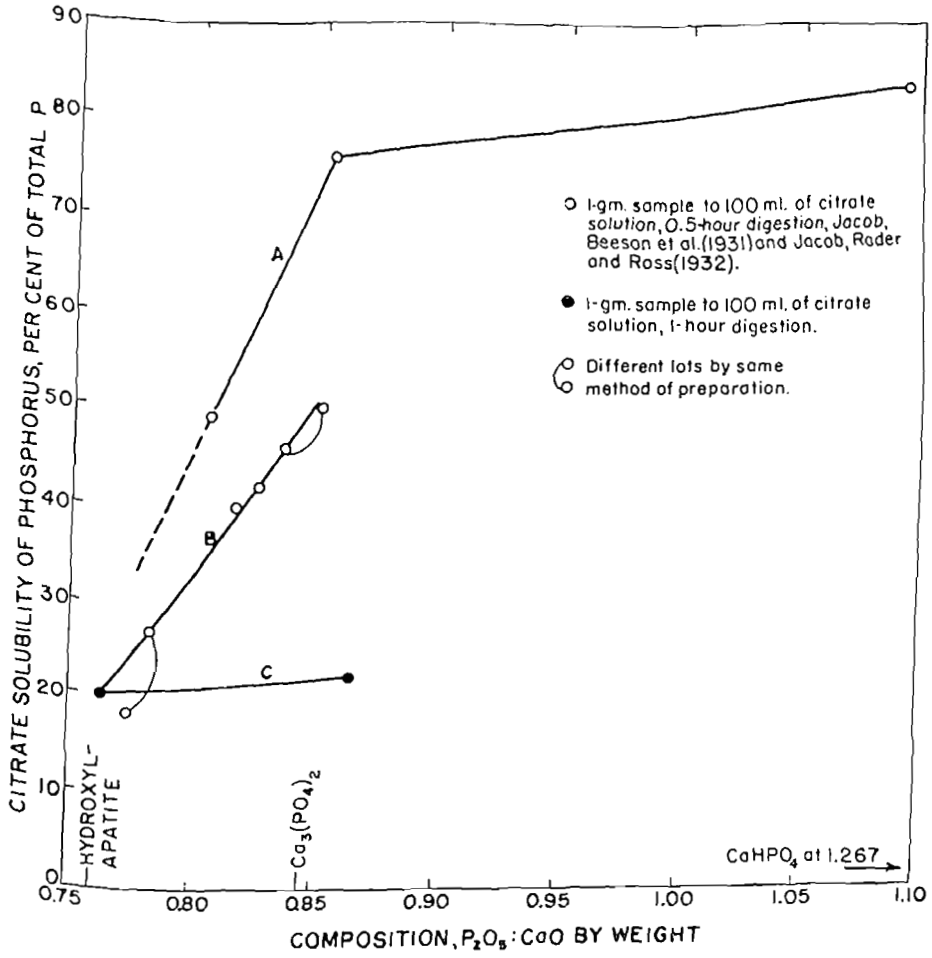


FIG. 3. Dependence of neutral citrate solubility of precipitated basic calcium phosphates on the chemical composition of the sample. Air-dried materials prepared by sundry methods.

and to possess a high degree of crystallinity. These aspects of the other materials were not determined. It will be noted that preparations with a calcium to phosphorus ratio near that of tricalcium phosphate present the widest observed spread in solubilities, which range from 22 to 76 per cent. The more soluble materials on this vertical may have con-

tained some dicalcium phosphate, but the equivalent mixture of hydroxylapatite and dicalcium phosphate, assuming the solubilities to be additive, would show a solubility of only about 50 per cent.

4. Presence of Other Salts

Many of the phosphate fertilizer materials are produced with a substantial complement of nonphosphorus compounds. Normal superphosphate carries calcium sulfate, ammonium phosphate usually contains more or less ammonium sulfate, and the products of nitric acid treatment of phosphate rock carry ammonium nitrate and/or calcium nitrate. When these materials are used in compounding complete fertilizers, potassium salts and other substances become a part of the assemblage of compounds. The associated salts influence the quality of the phosphate in one way or another—in some cases markedly, in others hardly at all. With some combinations reaction occurs, so that the mixture has to be cured for a period before it is ready for shipment to the consumer. For example, ammonium sulfate reacts with the monocalcium phosphate of superphosphate to form monoammonium phosphate and calcium sulfate. Thus the added compound is not necessarily the resident compound in the mixture. Even though chemical reaction does not take place, the solubility of the phosphate is often affected appreciably by the presence of other salts. For example, the water solubility of dicalcium phosphate is enhanced several fold by the presence of ammonium nitrate. These considerations emphasize the importance of the assemblage of compounds in the fertilizer as a determining factor of the quality of the phosphate component.

The disposition of the compounds with respect to one another in the mixture can influence the quality of the phosphate component. The effects stem from the character of the contacts between the compounds. The extent of the contact area between two component compounds is determined mainly by their finenesses, the thoroughness of dispersal, and the proportion of other components. The usual supposition is that compounds formed by reaction in the mixture are fine grained and well dispersed through the mixture. In some instances one component may envelop considerable quantities of another. A graphic example of this condition is furnace products that consist of crystals imbedded in glass. In the event the enveloping substance has the lower solubility, the observed solubility of the product is likely to be sensitive to the fineness of the sample. A somewhat similar condition obtains in granulated fertilizers as a consequence of the tendency for the more soluble compounds to concentrate in the surface crust of the granule during the drying operation.

III. Methods of Evaluation in the Laboratory

The first enterprise for producing superphosphate, undertaken by Lawes and Gilbert in England over 100 years ago, marks the beginning of chemically processed phosphate fertilizers. In the early years quality tests were concerned mainly with the more soluble part of superphosphate, since its superiority over untreated bone was attributed mostly, if not entirely, to the water-soluble phosphorus. Later on, the nutrient value of the water-insoluble fraction, or a part of it, of superphosphate and other chemically treated phosphates was recognized as being superior to that of the raw materials. From that time until the present the high quality of water-soluble phosphates has been generally accepted, and the major effort in the development of quality tests has been expended in studies of the water-insoluble phosphates. Numerous test procedures have been proposed and used to a greater or less extent. Of these a few have attained wide acceptance and are now classed as official methods either by statutory regulation or by common consent in nearly all countries.

In several countries of the world the laboratory evaluation of phosphate fertilizers is officially accomplished by means of one or more of the following chemical determinations:

Total phosphorus.
Water-soluble phosphorus.
Citrate-soluble phosphorus with use of neutral ammonium citrate solution, or alkaline ammonium citrate (Petermann, 1880).
Citric acid-soluble phosphorus with use of 2 per cent citric acid solution (Wagner *et al.*, 1903).

1. Official Methods

a. History. Soon after the establishment of the commercial fertilizer industry, agricultural chemists in Germany took the lead in the standardization of laboratory methods for evaluating phosphates, and as a result of their labors procedures were developed for evaluation with the use of citrate solutions, both neutral and alkaline, and citric acid solution.

With the founding of the Association of Official Agricultural Chemists (A. O. A. C.) in 1884, the development of official methods for analyzing phosphate fertilizers in the United States and Canada was organized on an orderly basis. The subject received major consideration at the first annual meeting (A. O. A. C., 1884), and it has continued to occupy a prominent place in the Association's work. Thus,

papers and reports relating to methods of phosphate analysis have been presented at 63 of the 65 annual meetings of the Association to 1951. The importance attached to methods for evaluating the quality of water-insoluble phosphorus is indicated by the fact that such methods received attention at no less than 56 of the meetings.

An excellent account of the world progress in methods of phosphate fertilizer analysis to about 1930 is given by Ross and Merz (1931). The principal developments to the present time are noted in the following paragraphs, with special reference to the United States.

1. Water-soluble phosphorus. During early years of the chemical fertilizer industry there were different views among chemists as to the correct manner of extracting fertilizers, especially superphosphate, for the purpose of determining water-soluble phosphorus, as pointed out by Stohmann (1864) and Fresenius (1868). In fact, most analysts had their own modifications, so that lack of agreement in their results was not uncommon. This situation led to the adoption of a standard method for water-soluble phosphorus in superphosphate at a meeting of German agricultural chemists, physiologists, and experiment station directors held in Dresden in 1871 (Anonymous, 1871). Modifications of the method were adopted at subsequent meetings in Germany, including one at Magdeburg in 1872 (Anonymous, 1873) and another at Halle in 1881 (Anonymous, 1882). Attendance at the Halle meeting comprised German experiment station directors, trade and technical chemists, and fertilizer manufacturers.

In the meantime, methods of phosphate analysis were being investigated in the United States by fertilizer control chemists and others, and a procedure for the determination of water-soluble phosphorus was adopted at the first annual meeting of the A. O. A. C. (1884). Further study led to the adoption in 1891 of a new procedure which specified that a 2-gram sample be washed with successive small portions of cold water to a filtrate volume of about 250 ml. No further major change was made until 1931, when the sample weight was reduced to 1 gram on the basis of evaluation studies on ammoniated superphosphate (Howes and Jacobs, 1931; Keenen, 1932; Ross and Jacob, 1931; Ross *et al.*, 1932).

2. Phosphorus soluble in neutral ammonium citrate solution. It appears that evaluation of water-insoluble phosphorus with the aid of ammonium citrate solutions was first suggested by Fresenius, Neubauer, and Luck (1871) in Germany. They showed that less than 2 per cent of the phosphorus in a finely ground, raw phosphate was dissolved when a 0.5-gram sample was digested at 30° to 35° C. in 50 ml. of neutral ammonium citrate solution (1.09 sp. gr.) for 0.5 hour with continuous

shaking. Under the same conditions, 95 per cent of the phosphorus in a sample of precipitated calcium phosphate was dissolved.

For the analysis of superphosphates these workers recommended that the water-insoluble residue from 2 grams of the material, prepared by washing the sample with cold water until the filtrate was no longer acid in reaction, be digested at 30° to 40° C. in 100 ml. of the citrate solution for 0.5 hour with shaking at very frequent intervals. The citrate-insoluble residue was washed two or three times with a mixture of equal parts of water and citrate solution and then analyzed for phosphorus. The citrate-soluble phosphorus was obtained indirectly by subtracting the sum of the water-soluble and citrate-insoluble phosphorus from the total phosphorus. An alternate procedure was to determine the citrate-soluble phosphorus directly by analysis of the citrate extract.

The method for citrate-insoluble phosphorus in fertilizers adopted at the first annual meeting of the A. O. A. C. (1884) was essentially the procedure proposed by Fresenius, Neubauer, and Luck for superphosphate, as outlined in the preceding paragraph, with the notable exceptions that the citrate digestion was made at 65° C. and the insoluble residue was washed with cold water alone. At the second meeting of the Association (1885, p. 14) it was recommended and adopted that so-called nonacidulated fertilizers be digested directly with citrate solution, without previous washing with water. On the basis of Haskins' (1920, 1921, 1922) studies, the provision with respect to nonacidulated fertilizers was modified in 1922 to permit the use of 1-gram samples of precipitated phosphates, specifically dicalcium phosphate. As a result of the previously mentioned studies of ammoniated superphosphates (Howes and Jacobs, 1931; Keenen, 1932; Ross and Jacob, 1931; Ross *et al.*, 1932), involving extensive laboratory and greenhouse investigations, this modification was extended in 1931 to other nonacidulated fertilizers, except basic slag, which was evaluated by the 2 per cent citric acid method, and to acidulated fertilizers, with the further provision that the time of the citrate digestion be increased from 0.5 hour to 1 hour.

At the 1943 meeting of the A. O. A. C., it was proposed by MacIntire *et al.* (1944) that manual shaking at 5-minute intervals during the citrate digestion, as specified in the official method, be replaced by continuous agitation with the aid of a mechanical device. Later, the use of continuous agitation was subjected to collaborative study (Jacob *et al.*, 1948, 1949) and was officially adopted as an alternative procedure in 1949.

The neutral ammonium citrate procedure was officially adopted for

the evaluation of basic slag at the 1949 meeting of the Association. At the same time the 2 per cent citric acid method was deleted from the official methods, and the neutral citrate procedure was made official for all phosphate materials and mixtures. These changes were based on the results of studies and investigations, both chemical and agronomic, conducted over a number of years by the Association (Ross and Jacob, 1937; Jacob *et al.*, 1947, 1949, 1950) and others.

3. *Phosphorus soluble in alkaline ammonium citrate solution.* Use of an alkaline solution of ammonium citrate for evaluation of the water-insoluble P_2O_5 in fertilizers was recommended by Joulie (1873) in France, about 2 years after Fresenius, Neubauer, and Luck (1871) proposed the use of neutral citrate for this purpose. At a meeting of agricultural experiment station directors held in Karlsruhe, Germany, in 1879, the results of numerous plant-growth experiments with various water-soluble and water-insoluble phosphates were presented by A. Petermann (1880), Gembloux station, Belgium, who proposed that the water-insoluble phosphorus in fertilizers be evaluated with the aid of an alkaline ammonium citrate solution (ca. 1.082 sp. gr. and 9.0 pH). Mohr (1884) recommended that the Petermann solution be used not only on superphosphate but also on precipitated phosphates, mixed fertilizers, and other products, with digestion of the sample at 60° to 70° C. instead of 35° to 38° C.

The Petermann method, in one form or another, is an official procedure in a number of countries, chiefly in Europe. It should be noted, however, that alkaline citrate methods have not been investigated or used to any extent in the United States.

4. *Citric acid-soluble phosphorus.* When basic slag was first introduced as a fertilizer in the early 1880's, the material was evaluated on the basis of its total phosphorus content and fineness. The need for other bases of evaluation soon arose, however, because of the temptation to adulterate the slag with raw phosphate rock. For this purpose, Wagner (1894, 1895) recommended a modification of a method based on the use of an acid ammonium citrate solution, which he had proposed earlier (Wagner, 1886) for the evaluation of superphosphate and precipitated phosphate. The modified method was used for a time by the association of German agricultural experiment stations for evaluating basic slag, and it is still used in China (Taiwan) as an alternative procedure for evaluating precipitated calcium phosphate.

Gerlach and Passon (1896) concluded that free citric acid, rather than ammonium citrate, was the principal active agent in Wagner's acid citrate solution, and they suggested that the ammonia could be omitted.

After numerous vegetation tests, Wagner (1899) proposed that basic slag be evaluated with the aid of a 2 per cent citric acid solution. The method, as described in detail by Wagner *et al.* (1903), involved placing 5 grams of ground slag in a 500-ml. flask containing 5 ml. of alcohol, filling the flask to the mark with 2 per cent citric acid solution at 17.5° C., rotating the tightly stoppered flask for 30 minutes in a machine turning 30 to 40 times per minute, immediately filtering the mixture, and analyzing the filtrate for phosphorus. This method was generally adopted and has continued to be an official procedure for the analysis of basic slag in most countries.

In 1911 the Association of Official Agricultural Chemists appointed a special committee to investigate the Wagner method. On the basis of numerous laboratory, greenhouse, and field tests it was concluded in the final report of this Committee (Haskins *et al.*, 1924) that the results obtained with the method reflect the quality of basic slag under the general conditions of its use as a fertilizer in the United States. The method was officially adopted for basic slag, and for this material only, by the Association in 1923 (Haskins *et al.*, 1923).

The work of Gerlach and Passon (1896), Hackl (1921), Wilhelmj *et al.* (1929), and others indicated that the neutral and alkaline citrate methods give much lower results on basic slag than does the 2 per cent citric acid method and that the citrate methods are not suitable for the analysis of slags. It has been shown, however, that the solubility of slag phosphorus in neutral ammonium citrate solution, for example, is quite sensitive to variations in the ratio of sample weight to solvent volume, as is generally true also of the phosphorus in other types of chemically processed, water-insoluble phosphates (Jacob *et al.*, 1931, 1932b, 1936). It was further shown (Jacob *et al.*, 1949) that, with a ratio of sample weight to solvent volume of 1 gram per 100 ml. and other conditions as specified in the official method for citrate-insoluble phosphorus in nonacidulated products (Association of Official Agricultural Chemists, 1950), the solubility of slag phosphorus in neutral citrate solution is close to its solubility in 2 per cent citric acid by the Wagner method. Accordingly, the 2 per cent citric acid procedure was discontinued as an official method of the A. O. A. C. at the meeting in 1949.

b. Analytical Procedures. The declaration of guarantees noted in Section V requires a group of seven phosphorus determinations consisting of total phosphorus and six fractional determinations, namely: water-soluble, citric acid-soluble, neutral citrate-soluble, alkaline citrate-soluble, water- and neutral citrate-soluble, and water- and alkaline citrate-soluble. The latter two determinations differ from the two

immediately preceding ones, respectively, in that the sample is washed with water and the water-insoluble residue is digested with the citrate solution; the soluble phosphorus is then determined (1) directly on the combined water and citrate extracts, or (2) by difference between the total and the citrate-insoluble phosphorus.

The official procedures used in the United States, Canada, and Mexico are those of the Association of Official Agricultural Chemists (1950). The Association's methods or adaptations thereof are also used wholly or in part by a number of other countries, including Chile and some of the Australian and Brazilian states. The methods used in 14 countries of western Europe are outlined in a recent publication of the Organization for European Economic Co-operation (1952).

Fortunately, the extraction procedures are defined by a relatively small set of important stated conditions, which afford a basis for com-

TABLE IV

PROPERTIES AND PERFORMANCE OF REAGENTS USED FOR EXTRACTION OF SOLUBLE PHOSPHORUS FROM FERTILIZERS IN OFFICIAL TESTS OF QUALITY

A. Properties[a]

Reagent solution	*Specific gravity (temp., °C.)*	*pH*	*Concentration*	
			Per cent by weight	*Molarity of citrate ion*
Citric acid ($H_3C_6H_5O_7 \cdot H_2O$) (Wagner)	1.007 (15)	2.0[b]	*2	0.095
Neutral ammonium citrate	*1.09 (20)	*7.0	20	0.88
Alkaline ammonium citrate (Petermann)	*1.08[c] (15)	9.0[b]	20	0.84

B. Performance on Fertilizers[b,d]

Reagent solution	*Soluble phosphorus (per cent of total P) found in—*		
	Fused tricalcium phosphate, —100 mesh	*Ammoniated superphosphate, 4 per cent NH_3*	
		Prior water wash	*Without water wash*
Citric acid	82	..	..
Neutral ammonium citrate	79	83	77
Alkaline ammonium citrate	55	70	65

[a] Specified properties are marked with an asterisk; others are estimated.

[b] Determined by J. H. Caro, Bureau of Plant Industry, Soils, and Agricultural Engineering.

[c] The specifications require the specific gravity to be 1.082 to 1.083 and 1 ml. to contain 0.042 gram of N.

[d] Digestion with citric acid was with continuous agitation; citrate digestion was with periodic agitation (A. O. A. C. procedure).

parison. The conditions to be considered here are: extractant, fineness of sample, sample weight, sample-solvent ratio, and mode of performing extraction, including technique (repeated extraction, trituration, etc.), additives, such as wetting agents, filter paper, etc., type of agitation, temperature, and duration. Some properties of the three reagents containing citrate ion are given in Table IV. The performance of these extractants on two typical phosphate fertilizers is shown in Table IV. Perhaps the chief point of interest lies in the comparison between citrate solutions. It should also be noted that the results obtained on ammoniated superphosphates by both solutions are influenced noticeably by prior washing with water. The effect of water washing on neutral citrate solubility was studied by Jacob *et al.* (1936).

Specifications for the preceding list of conditions, classified according to the six ways of fractionating the phosphorus, are summarized for several countries in Tables V and VI. Each specification is listed only once regardless of the number of procedures containing it. Hence, the summary shows the variability of any one of the conditions among procedures, but not the frequency of a particular specification. The outstanding feature displayed by this summarization is the great variability among procedures using the same extractant. The procedure for water-soluble phosphorus and those depending on alkaline citrate solution show the greater variability—a circumstance that perhaps reflects their wide use.

c. Procedure Execution. Variations in stated specifications were considered in the preceding section. A matter of greater practical importance is variation in the execution of a particular procedure embodying one of the general methods for fractionating the phosphorus in fertilizers, for example, the neutral citrate method as it is applied to water-insoluble phosphates in the United States. It is hardly necessary to note that good reproducibility of results both within and among laboratories depends on uniformity of execution of the procedure and that the basis of significant deviations must be sought among the conditions obtained in practice.

Procedure execution is intimately related to the procedure itself. Stated conditions must be attainable by reasonably simple means and at the same time susceptible to uniformity of application. Some conditions are critical, whereas others are not. The critical ones are often called factors. The ideal in procedure design is to specify only critical conditions. However, a difficulty lies in the circumstance that a condition found unimportant for one material may be critical for another. Continuous agitation is an example (Jacob *et al.*, 1936, 1948, 1949, 1950, 1951; MacIntire *et al.*, 1944). Furthermore, certain critical con-

TABLE V

CONDITIONS SPECIFIED IN SEVERAL COUNTRIES FOR EXTRACTION OF SOLUBLE PHOSPHORUS FROM FERTILIZERS WITH WATER ALONE AND WITH CITRIC ACID SOLUTION[a]

Condition	*Water-soluble phosphorus*[b,c]		*Citric acid-soluble phosphorus*[b]
Fineness of sample	ns, ar, pwdr; −20, −30, −35 m; 0.5, 1, 1.5, 2 mm	(−20, −35 m)[c]	ns, ar; −20, −35, −100 m; 0.5, 1, 1.5, 2 mm
Sample weight, grams	ns, 1, 1.5, 2, 2.5, 5, 10, 20	(1)	ns, 2.5, 5
Sample-solvent ratio, grams/ml.	1/40, 1/80, 1/90, 1/100, 1/125, 1/160, 1/200, 1/250	(1/250)	ns, 1/100
Extraction:			
Technique	FV, FVT, RE, RE on filter	(RE on filter)	FV
Additive	none	(none)	ns, alc
Agitation	ns, none, C, C + P	(none)	C
Temperature, °C.	r, r and 80	(r)	r, 17.5, 15–18, 16–19, 20–25, 17.5 to r, 30 to r
Duration, hours	ns, 0.5, 1, 2, 0.5 + 24, 2 + 24	(ns)	0.5

[a] Compiled, with the assistance of Mildred S. Sherman, from the sources indicated in Table XII, footnote *a*. The materials to which the solubility determinations are applied in the several countries are indicated in Table XII.

[b] Abbreviations for specified conditions:

In all places: ns, not stated.

Fineness of sample: ar, sample as received; pwdr, finely ground; mm, millimeter; m, mesh per linear inch.

Extraction:

Technique: FV, fixed volume of solvent; FVT, same with trituration; RE, repeated treatment; RET, same with trituration

Additive: alc, alcohol; fp, filter paper.

Agitation: C, continuous; P, periodic.

Temperature: r, room temperature.

[c] Specifications in parentheses are those used in the United States, Canada, and Mexico.

TABLE VI

CONDITIONS SPECIFIED IN SEVERAL COUNTRIES FOR EXTRACTION OF SOLUBLE PHOSPHORUS FROM FERTILIZERS WITH CITRATE SOLUTIONS[a]

Condition	*Solubility determined with use of*		
	Neutral citrate solution[b,c]		*Alkaline citrate solution*[b]
Citrate-soluble phosphorus[d]			
Fineness of sample	−20, −30, −35, −100 m; 0.5, 1, 2 mm	(−20, −35 m)[c]	ns, pwdr; 1, 1.5, 2 mm
Sample weight, grams	ns; 1, 5; 0.1–0.4 of total P_2O_5	(1)	ns, 0.75, 1, 2.5
Sample-solvent ratio, grams/ml.	1/25, 1/50, 1/100, 1(P_2O_5)/1,000	(1/100)	1/80 (+H_2O), 1/100, 1/200
Extraction:			
Technique	FV	(FV)	ns, FV, FVT, RE, RET
Additive	ns, fp	(fp)	ns, fp, glass
Agitation	C + P, C or P, P	(C or P)	ns, C, P
Temperature, °C.	cool and 35–40, r and 65, 65	(65)	ns, r, r and 40, 40, 60
Duration, hours	0.5, 1, 3 + 1, 24 + 1	(1)	1, 3, 3+, 4, 15 + 1, 18 + 1, 3 + overnight + 3, 0.5 + 15 + 1
Water- and citrate-soluble phosphorus[e]			
Fineness of sample	−20, −35, −100 m; 0.5, 1, 2 mm	(−20, −35 m)[c]	ns, pwdr; 1, 1.5, 2 mm
Sample weight, grams	1, 2, 2.5, 5	(1)	ns, 1, 1.5, 2, 2.5, 4
Sample-solvent ratio, grams/ml.	1/20, 1/40, 1/50, 1/100	(1/100)	ns, 1/25, 1/40, 1/50, 1/100
Extraction:			
Technique	FV	(FV)	ns, FV, FVT
Additive	fp	(fp)	ns, fp
Agitation	C (at start), C + P, C or P, P	(C or P)	ns, none + P, P (at start only), P
Temperature, °C.	35–40, 65	(65)	ns, r, r and 40, 40, 60
Duration, hours	0.5, 1	(1)	3, 4, 1 + 12, 15 + 1, 18 + 1

[a] Compiled, with the assistance of Mildred S. Sherman, from the sources indicated in Table XII, footnote *a*. The materials to which the solubility determinations are applied in the several countries are indicated in Table XII.

[b] The abbreviations are defined in Table V, footnote *b*.

[c] Specifications in parentheses are those used in the United States, Canada, and Mexico.

[d] The sample is extracted directly with citrate solution.

[e] The water-insoluble residue is extracted with citrate solution.

ditions cannot by any practical means be maintained constant throughout the fractionation process, and consequently the specifications refer only to the initial conditions. Some initial conditions can be simply defined in nominal terms only. Thus the nominal conditions together with numerous unspecified conditions constitute a set of ambient conditions that are responsible for the uncontrolled variation in procedure execution.

Among the specified conditions mentioned in the preceding section, digestion temperature is maintained constant for the duration of the digestion. Solvent pH and concentration, additive, sample weight, and sample-solvent ratio are constant initial conditions. Fineness of sample and type of agitation are nominal conditions. Since sample weight and sample-solvent ratio refer to the material under test, the phosphorus-solvent ratio, which is perhaps the critical condition, varies with the phosphorus content of the sample. The mean particle size of different grinds of a material often varies considerably within the range below the specified sieve.

Each laboratory has established practice for the routine performance of general operations. This customary way of doing laboratory work contributes in a considerable measure to uniformity in procedure execution as regards many of the ambient conditions. Accordingly, critical conditions not specified in the procedure may be controlled automatically within sufficiently narrow limits. However, this automatic control of ambient conditions, and with it also procedure execution, varies more or less from place to place. For this reason the reproducibility of results among laboratories is not ordinarily as good as that enjoyed within a laboratory. The conditions specified in the neutral citrate procedure, as well as numerous other pertinent conditions, have been investigated more or less extensively with a view towards determining their influence on the analytical result and finding the most effective specification for minimizing their effects on reproducibility (Adams and Ross, 1938; Howes and Jacobs, 1931; Jacob and Tremearne, 1937; Jacob *et al.*, 1932a, 1936, 1948; MacIntire and Hardin, 1935; MacIntire *et al.*, 1935, 1944; Ross and Adams, 1939; Ross and Hardesty, 1936; Ross *et al.*, 1932). The success of these efforts is perhaps best indicated by the agreement of results now attainable among laboratories, which is illustrated by some examples selected from a recent collaborative study and presented in Table VII.

d. Application to Different Materials. When the procedure is applied to different materials, composition in all its aspects (Section II) constitutes an important set of ambient conditions, which, being capable of rather wide ranges of variation, render physical interpretation of the

TABLE VII

SOLUBLE PHOSPHORUS FOUND IN SOME TYPICAL FERTILIZERS BY DIFFERENT ANALYSTS IN A COLLABORATIVE STUDY[a]

Phosphate material	*Fineness, mesh*	*Total P_2O_5, per cent*	*Soluble phosphorus,[b] per cent of total P*	
			Range	*Average*
Ammoniated superphosphate[c]	− 40	21.0	90.1–97.0	92.9
Ammoniated superphosphate[d]	− 40	19.7	84.1–92.0	87.9
Mixed fertilizer, 4–12–6[e]	− 40	12.3	95.9–99.1	97.9
Fused tricalcium phosphate	−100	27.7	80.9–84.1	82.3
Phosphate rock–Mg silicate glass	−100	20.4	82.8–95.0	90.3
Florida land-pebble rock	−100	30.8	9.9–13.5	10.8

[a] Results were calculated from data given by Jacob *et al.* (1948).
[b] Determined in 7 to 8 laboratories with use of continuous end-over-end agitation during the citrate digestion.
[c] Total N 3.45 per cent.
[d] Total N 4.87 per cent.
[e] Formulated with ammoniated superphosphate containing 4.87 per cent N, ammonium sulfate, potassium chloride, dolomite, Hyperhumus, and sand filler.

results for soluble phosphorus generally difficult and in many cases next to impossible. The physical significance of the soluble phosphorus found in single well-defined compounds can be strongly inferred from solubility product considerations (Fig. 1). Similarly, though with less confidence, the significance of the soluble phosphorus in assemblages of well-defined phosphate compounds can be inferred qualitatively from the principle of common-ion effects. In the case of fertilizer materials, where amorphous phosphates are present (or at least cannot be ruled out) with crystalline phosphates, soluble phosphorus—not being assignable entirely to definite compounds of known characteristics—must be viewed in a very general way. The situation is still more complex in mixed fertilizers, which for obvious reasons cannot be considered in this discussion.

Although the soluble phosphorus in fertilizer materials generally cannot be related entirely to definite compounds, it can nearly always be given a firm interpretation by experimentally relating it to some other property of the material. Thus, the citrate solubility of calcined (1400° C.) phosphate rock was found to depend on the extent of fluorine volatilization from the products, and the limiting conditions have been determined (Reynolds *et al.*, 1935). This method of handling fertilizer materials is further illustrated by the solubility-fineness relationship for calcium metaphosphate glass and for other furnace products (Figs. 2 and 3). Another illustration is afforded by the work on ammoniated superphosphate (Hardesty *et al.*, 1943; Keenen, 1930, 1932; Ross and

Jacob, 1931; Ross *et al.*, 1932; White *et al.*, 1935), the findings of which are discussed in the following paragraphs.

The changes that occur in superphosphate when it is ammoniated are customarily described by writing chemical equations for the separate reactions. For the present purpose, however, the pertinent facts can

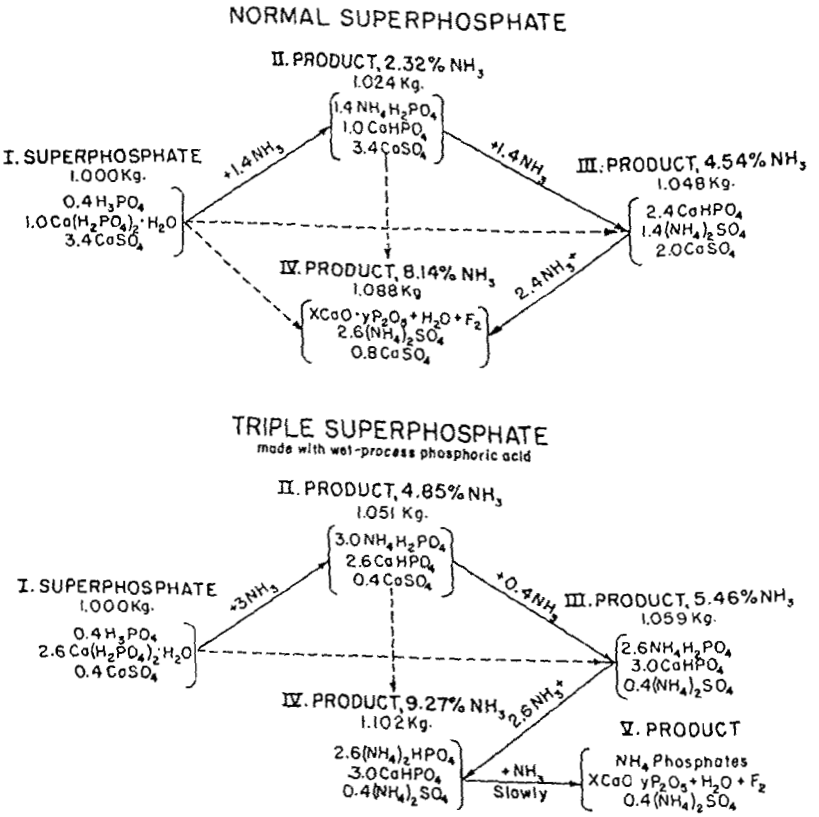


FIG. 4. Critical assemblages of compounds occurring in stepwise neutralization of normal and triple superphosphate with ammonia. Ideal sequence is shown by solid arrows, possible short-circuit reactions by broken arrows; composition of superphosphate approximates actual material, and percentages of ammonia are based on mixture without loss by evaporation; number preceding formula is moles of compound per kilogram of initial superphosphate.

be presented more compactly and with greater clarity with the use of critical assemblages of the principal participating compounds as they would appear under ideal conditions at the completion of the respective stages of neutralization. The sequence of such assemblages occurring during the ammoniation of normal and triple superphosphates is shown

in Fig. 4. Among the participating compounds phosphoric acid, monocalcium phosphate, and the ammonium phosphates are water-soluble, dicalcium phosphate is citrate-soluble, and the undefined basic phosphate is partially citrate-soluble. Accordingly, the amount of soluble phosphorus that would be expected in the ammoniated products on the basis of the compounds composing the critical assemblages can be written down at once (Table VIII).

TABLE VIII

SOLUBLE PHOSPHORUS IN ASSEMBLAGES OF FIGURE 4 AS PREDICTED FROM THE NATURE OF THE COMPOUNDS

Assemblage	*NH_3 in product, per cent*	*Soluble PO_4, moles per kilogram of initial superphosphate*		
		Water-soluble	*Citrate-soluble*	*Available*
		Normal superphosphate		
I	0.0	2.4	0.0	2.4
II	2.32	1.4	1.0	2.4
III	4.54	0.0	2.4	2.4
IV	8.14	0.0	Undefined[a]	Undefined[a]
		Triple superphosphate		
I	0.0	5.6	0.0	5.6
II	4.85	3.0	2.6	5.6
III	5.46	2.6	3.0	5.6
IV	9.27	2.6	3.0	5.6

[a] The solubility of similar, though fluorine-free, materials is shown in Fig. 3.

In the case of normal superphosphate the results (Table VIII) indicate that water-soluble phosphate compounds should be converted into water-insoluble citrate-soluble compounds, without sensible loss of available phosphorus, at about 4.5 per cent ammonia. Application of the procedure for water- and citrate-soluble phosphorus would, however, show some water-soluble phosphorus derived from the normal solubility of dicalcium phosphate as enhanced by the presence of ammonium salts. At still higher percentages of ammonia, the formation of basic phosphate can be expected to result in a lowered phosphorus solubility. The extent to which these deductions agree with experiment is illustrated by the data in Fig. 5. Here the water-soluble phosphorus decreased with ammoniation, though less rapidly than the prediction, up to above 6 per cent ammonia. At the same time the formation of

citrate-soluble phosphorus above 2.2 per cent ammonia, which corresponds with assemblage II (Table VIII) showed a marked sensitivity to reaction temperature. That the higher temperatures favor the short-circuit reactions (Fig. 4) is strongly indicated. With allowance for

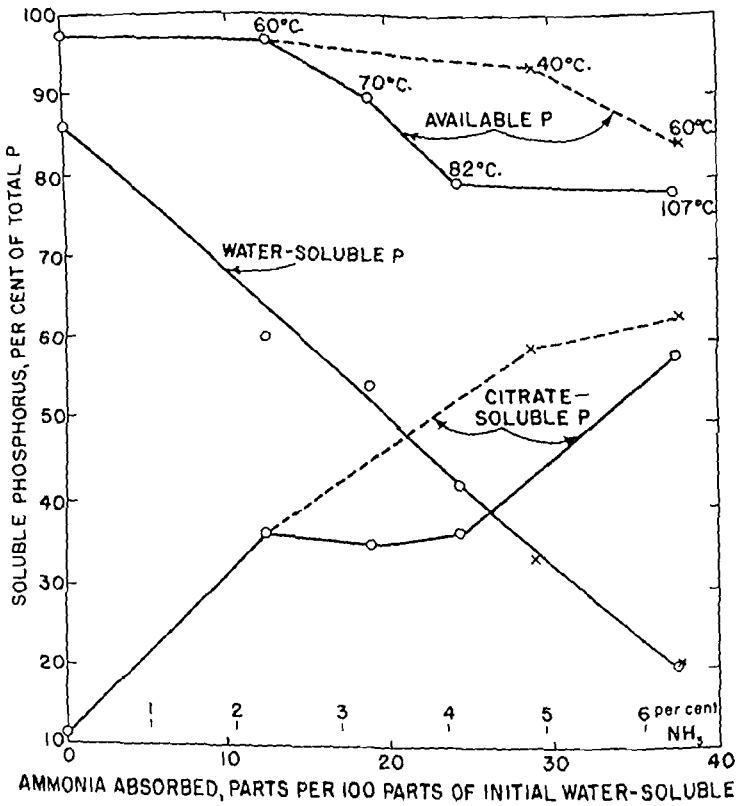


Fig. 5. Dependence of phosphorus solubility of ammoniated superphosphate on amount of ammonia absorbed—normal superphosphate. Maximal temperature during ammoniation is shown on curves for available P. (Unpublished results of J. O. Hardesty and R. Kumagai, Bureau of Plant Industry, Soils, and Agricultural Engineering.)

temperature effects, the experimental results agree with the deductions from the nature of the assemblages.

According to the results for the sequence of assemblages in ammoniated triple superphosphate (Table VIII), the water-soluble phosphorus should decrease to an intermediate value while the citrate-soluble phosphorus increases to an intermediate value at about 4.9 per cent ammonia, and thereafter both should remain steady without loss of avail-

able phosphorus over the range 4.9 to about 9.3. In this instance the experimental results (Fig. 6) are in almost perfect agreement with the predicted solubility behavior.

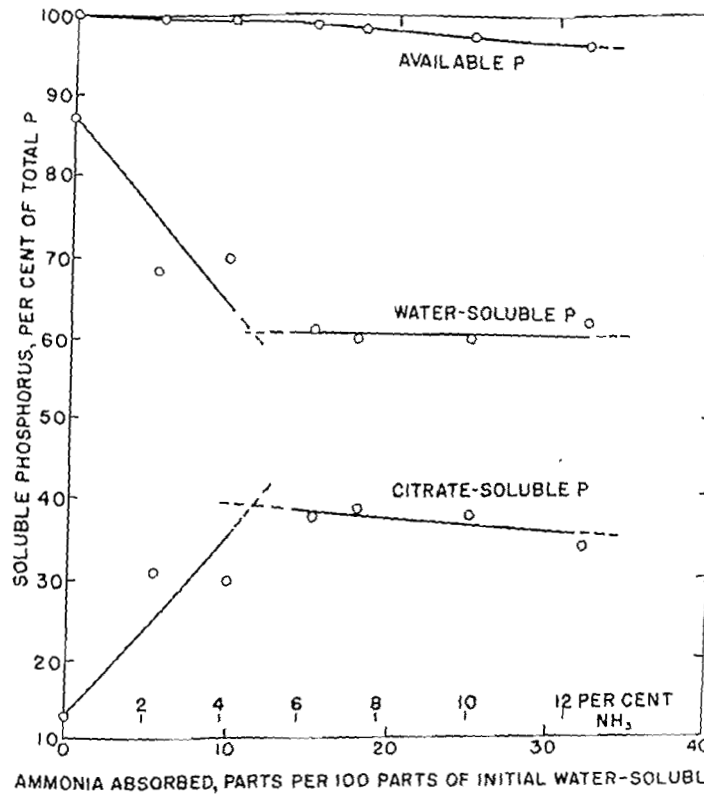


FIG. 6. Dependence of phosphorus solubility of ammoniated superphosphate on amount of ammonia absorbed—triple superphosphate. (White *et al.*, 1935.)

2. *Other Methods*

A number of laboratory methods that have not gained official status for evaluating phosphate fertilizers have been proposed and studied from time to time. They may be classed in two groups: (1) solubility methods, based on the use of various solvents; and (2) biological methods, which involve determination of the relative effectiveness of the phosphates in supplying phosphorus for nutrition of certain seedling plants and soil organisms.

a. Solubility Methods. As previously mentioned, Wagner (1886, 1894, 1895) recommended the use of acid ammonium citrate solution for evaluating superphosphate, precipitated phosphate, and basic slag.

A wide variety of other reagents have been proposed for the evaluation of water-insoluble phosphates. The list includes carbonic, nitric, sulfuric, acetic, formic, humic, lactic, oxalic, and tartaric acids and solutions of potassium acid sulfate, ammonium humate, ammonium oxalate, ammonium tartrate, sodium citrate, and citrated ammonium nitrate.

MacIntire, Shaw, and Hardin (1938) proposed a method involving the use of a citrated ammonium nitrate solution (pH 4.2). The method appears to have the principal advantage that the soluble (available) phosphorus is determined directly, rather than by difference—total phosphorus minus citrate-insoluble phosphorus—as in the method of the Association of Official Agricultural Chemists (1950). It should be noted in this connection that direct determination of the soluble phosphorus is also specified in the official citrate procedures used by a number of countries (Organization for European Economic Co-operation, 1952). Recent studies by Allen *et al.* (1952) indicate that this may also be done with the A. O. A. C. method. A collaborative study authorized by the Association and made by Ross and Rader (1940) and Rader and Ross (1941) did not culminate in a recommendation for adoption of the MacIntire-Shaw-Hardin method.

b. Biological Methods. It has been proposed to evaluate phosphate fertilizers on the basis of their ability to supply phosphorus for the nutrition and functioning of nitrogen-fixing bacteria in laboratory cultures. Thus, Truffaut and Bezssonoff (1927) reported that chemically processed phosphates are far more effective in this respect than are the parent phosphate rocks. Guittonneau (1929) found differences in the effects of various phosphate fertilizers on the development of *Azotobacter*. According to Niklas *et al.* (1926) the effect of different phosphates, as shown by the magnitude of the optimal addition, can be correlated with the chemical solubilities of the phosphates in different solvents. Citrate-soluble phosphorus is said to be more effective than citric acid-soluble phosphorus in promoting the development of *Azotobacter* (Strobel and Scharrer, 1926). Using the plaque method of Sackett and Stewart (1931), Joshi and Ayyar (1934) found that synthetic tricalcium phosphate, superphosphate, and solubilized bone products induced good to excellent growth of *Azotobacter* in all the soils tested, whereas apatite produced no growth and finely ground phosphate rock gave variable results.

Mehlich (1937) and Mooers (1938) have evaluated phosphate fertilizers on the basis of their effectiveness in supplying phosphorus for the nutrition of the fungus *Cunninghamella blakesleeana*. The average relative values obtained by Mooers in tests of the effect of eight phosphate materials on growth of the fungus in five types of Tennessee silt

and sandy loam soils are given in Table IX. As reported by Mehlich (1937), the pH values of the soils ranged from 5.2 to 6.5.

TABLE IX

AVERAGE EFFECTIVENESS OF DIFFERENT PHOSPHATES AS DETERMINED BY THE CUNNINGHAMELLA AND NEUBAUER METHODS WITH FIVE TYPES OF TENNESSEE SILT AND SANDY LOAM SOILS[a]

Phosphate	*Relative value*	
	Cunninghamella	*Neubauer*
Monocalcium phosphate	100	100
Triple superphosphate	96	74
Dicalcium phosphate	87	92
Fused phosphate rock[b]	81	97
Calcium metaphosphate[c]	70	64
Tricalcium phosphate	52	60
Calcium metaphosphate[d]	43	18
Phosphate rock	6	18

[a] Mooers (1938).
[b] Fused tricalcium phosphate.
[c] Relatively high in water-soluble phosphorus (Mooers, 1938).
[d] Low in water-soluble phosphorus (Mooers, 1938).

Among the laboratory biological procedures for evaluating phosphate fertilizers, the rye seedling method of Neubauer (Neubauer and Schneider, 1923) has received by far the most attention (Behrens, 1938; Dreyspring *et al.*, 1929; McGeorge, 1939; Mooers, 1938; Rauscher, 1927; Scharrer and Schreiber, 1940; Thornton, 1931, 1932, 1935; Thun, 1939). In soil media the order of effectiveness of different phosphates in supplying the phosphorus requirements of seedling plants and fungi may vary considerably with the pH and other soil characteristics.

As reported by Mooers (1938), the data of Table IX indicate medium to high ratings for triple superphosphate, dicalcium phosphate, and fused phosphate rock, in comparison with monocalcium phosphate, by both the Neubauer and the *Cunninghamella* methods. Lower ratings are indicated for calcium metaphosphate, tricalcium phosphate, and especially phosphate rock.

Thornton (1932) made Neubauer tests on a number of ammoniated superphosphates and other phosphates. The materials had been used in pot tests at 11 agricultural experiment stations with 8 crops on soils having pH values below 6 (Ross *et al.*, 1932). The results obtained by both test methods are summarized in Table X. In general, the ratings by the biological tests were higher, often considerably higher, than the availability ratings by the neutral ammonium citrate method, but most

TABLE X

QUALITY OF PHOSPHORUS IN SOME PHOSPHATE MATERIALS AS SHOWN BY SOLUBILITY, NEUBAUER, AND POT TESTS[a]

Sample No.	Phosphate	Available P, per cent of total P[b]	Relative nutrient value of P[c]	
			Neubauer method[d]	Pot tests[e]
B-1	Monocalcium phosphate	100	100	100
A-1	Superphosphate, normal[f]	98	99	111
A-10	Ammoniated superphosphate,[g] 2.48% NH_3	93	106	89
A-11	Ammoniated superphosphate,[g] 5.36% NH_3	96	112	102
A-12	Ammoniated superphosphate,[g] 6.83% NH_3	80	108	77
A-13	Ammoniated superphosphate,[g] 8.66% NH_3	67	105	92
B-2	Dicalcium phosphate	100	93	94
B-3	Tricalcium phosphate, hydrated	72	104	94
B-7	Hydroxylapatite, synthetic	28	66	84
B-8	Basic slag, imported	79	103	112
B-9	Bonemeal, steamed	45	85	99
B-11	Basic slag, fluorspar	18	6	36
B-12	Bone ash	10	3	29
B-14	Phosphate rock, Tennessee-brown	7	18	12
B-15	Fluorapatite, mineral	2	10	−6

[a] Ross *et al.* (1932), Thornton (1932).
[b] Determined with periodic shaking during neutral citrate digestion.
[c] Referred to monocalcium phosphate.
[d] A silt loam soil, pH 5.4, was used.
[e] On soils with pH values below 6.
[f] Made from Florida land-pebble phosphate.
[g] Made by ammoniating superphosphate A-1 with anhydrous ammonia.

of the materials that had phosphorus availabilities of less than 50 per cent were given very low ratings by the biological tests. It should be mentioned that, in pot tests with these materials on soils having pH values above 6, the relative nutrient values of the ammoniated superphosphates and the water-insoluble phosphates were generally lower than those on soils having pH values below 6 (Ross *et al.*, 1932).

IV. Available Phosphorus as an Index of Nutrient Value

Implied in the subject of this section is the unavoidable necessity for drawing comparisons between two different measures of fertilizer quality. Considerable discussion has been devoted to methods for determining phosphorus solubility and to the interpretation of its physical significance in relation to a number of fertilizer materials. In order to develop close comparisons of this solubility with the nutrient value

determined by vegetation tests, some procedure for measuring nutrient value must be selected. Perhaps it is unfortunate that an accepted method for the determination of nutrient value, possessing the force of an official method, has not been developed.

Procedures for vegetative tests also involve specifications as to conditions—constant, initial, and nominal. Curiously enough, for most conditions mentioned in connection with solubility methods analogous ones can be found in vegetative testing; for example, fertilizer type and soil type, phosphorus content and phosphorus level, volume of extractant and moisture level, sample-solvent ratio and rate of application, technique for contacting sample with solvent and fertilizer placement, and duration of digestion and growth period. The level of control that is, or can be, maintained over them is a matter for others to decide. For the immediate purpose at hand, practical considerations dictate that the method for determining nutrient value should permit control of the largest possible number of critical conditions; this restricts the comparisons to nutrient values determined by greenhouse procedures.

In the illustrative comparisons yield response is used as the measure of nutrient value. Results are given for ammoniated superphosphate, defluorinated phosphate rock (calcined and fused), calcium metaphosphate glass, and phosphate rock.

1. Ammoniated Superphosphate

In recent work Martin *et al.* (1953) grew lettuce on four acid and two calcareous California soils fertilized with normal superphosphate and two ammoniated superphosphates (2.5 and 5.5 per cent NH_3). The available phosphorus was 93 to 97 per cent of the total. Their results for an acid soil are shown in Fig. 7, their averaged results for the calcareous soils in Fig. 8.

On the acid soil the three superphosphates showed significant differences (19:1) in only 2 of 48 comparisons. The response appears to depend on the available phosphorus rather than on the water-soluble fraction. In this connection the heavily ammoniated superphosphate has a special interest. Interpolation on the curve for the dependence of solubility on the ammonia absorbed (Fig. 5) shows that the water solubility of the available phosphorus should be 30 to 37 per cent; it was actually 30 per cent by analysis.

On the calcareous soils (Fig. 8) normal and lightly ammoniated superphosphate gave almost identical yields at all application rates, and the yield response was about the same as that on acid soil. On the other hand, heavily ammoniated superphosphate gave much lower yields, and this indicates that the response is related to the water-soluble part

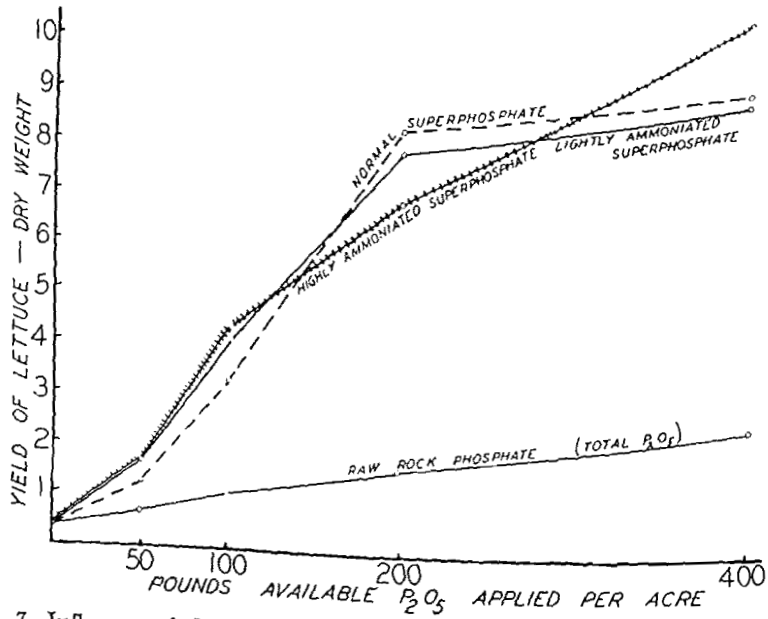


FIG. 7. Influence of degree of ammoniation of normal superphosphate on yield of lettuce grown on Rocklin sandy loam soil (pH 5.6) in greenhouse. Growth period 4 to 6 weeks. (Martin *et al.*, 1953.)

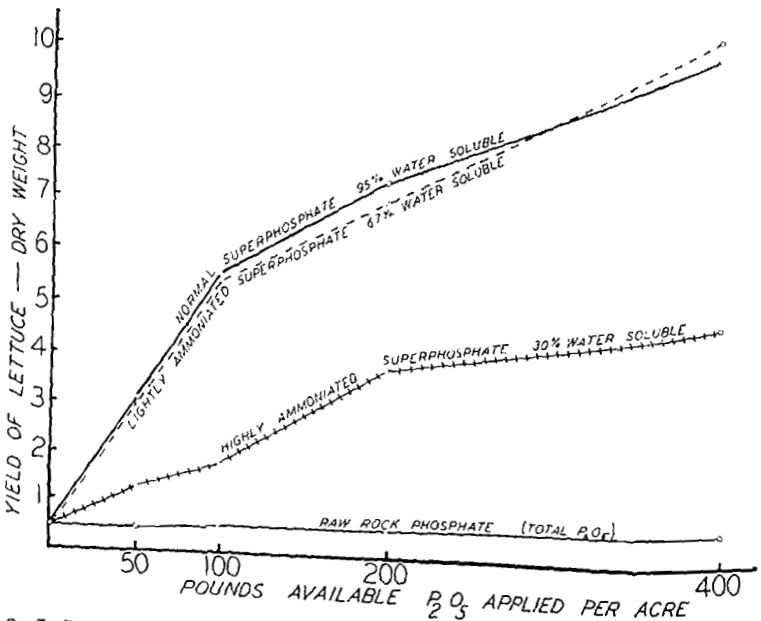


FIG. 8. Influence of degree of ammoniation of normal superphosphate on yield of lettuce grown on calcareous soil in greenhouse. Growth period 4 to 6 weeks; results on two soils (pH 7.9 and 8.0), not being significantly different, were averaged. (Martin *et al.*, 1953.)

of the available phosphorus, which is in agreement with the recognized superiority of water-soluble phosphate on calcareous soil.

2. *Defluorinated Phosphate Rock*

a. Calcined Phosphate. The relationship between the extent of fluorine volatilization and the citrate solubility of partially defluorinated phosphate was noted in Section III.1.d. A parallel relationship also

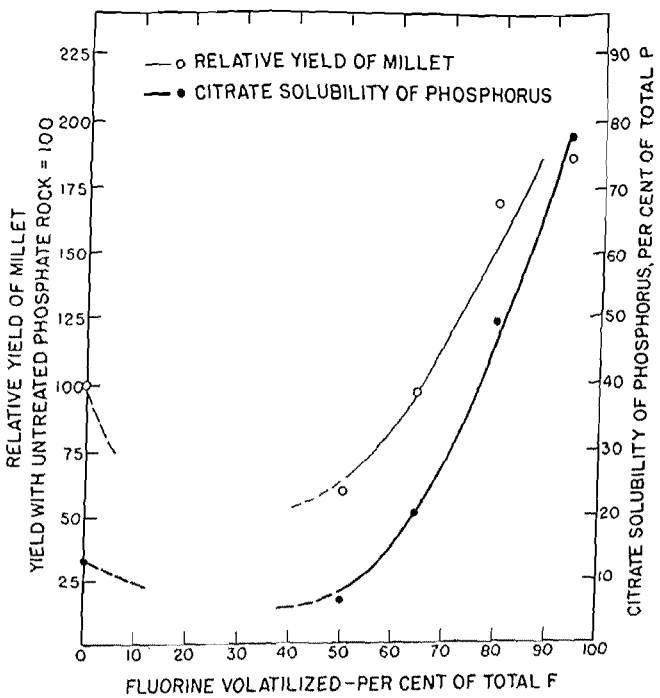


FIG. 9. Influence of degree of defluorination of Florida land-pebble phosphate on neutral citrate solubility of phosphorus (intermittent agitation during citrate digestion) and on yield response of millet grown on Norfolk loamy fine sand soil in greenhouse. Results of Brown *et al.* (1934) for 240 lb. of total P_2O_5 per acre from 100-mesh phosphate mixed with all the soil; growth period 69 days.

exists between fluorine volatilization and the nutrient value of the product. Both relationships are depicted in Fig. 9.

b. Fused Tricalcium Phosphate. This defluorinated product differs from calcined phosphate mainly in that it contains considerably more phosphate-bearing glass. Its citrate solubility depends markedly on fineness of the sample (Fig. 2), and the nutrient value shown by crop yield also varies with fineness in a closely agreeing pattern, as shown in Fig. 10.

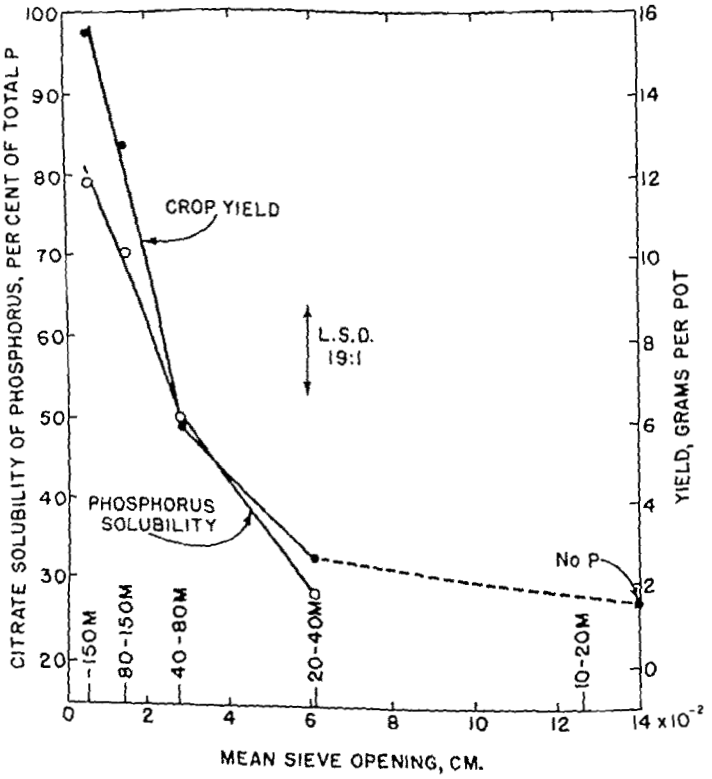


FIG. 10. Influence of particle size of fused tricalcium phosphate on neutral citrate solubility of phosphorus (intermittent agitation during citrate digestion) and on yield response of millet grown on Evesboro sandy loam soil in greenhouse. Results of Armiger *et al.* (1945) for 75 lb. of total P_2O_5 per acre mixed with upper third of soil; growth period 40 days.

3. *Calcium Metaphosphate Glass*

During the past few years calcium metaphosphate glass has been studied rather extensively in collaborative work on improvements in the official procedure for determining available phosphorus and also on its own merits. The product is the only all-glass phosphate material that is potentially an acid phosphate. It can thus be used in mixtures with ammonium salts without danger of ammonia losses. Since it is sensibly water-insoluble in the fertilizer sense and also a glass, its solubility in citrate solution shows dependence on particle size (Fig. 2). Crop response to it at low rates of application likewise depends on the fineness of material. Both relationships are depicted in Fig. 11. It will be noted that solubility determined with the use of periodic agitation follows growth response very well, whereas the solubilities obtained with the use of continuous agitation lie well above the growth curve. This

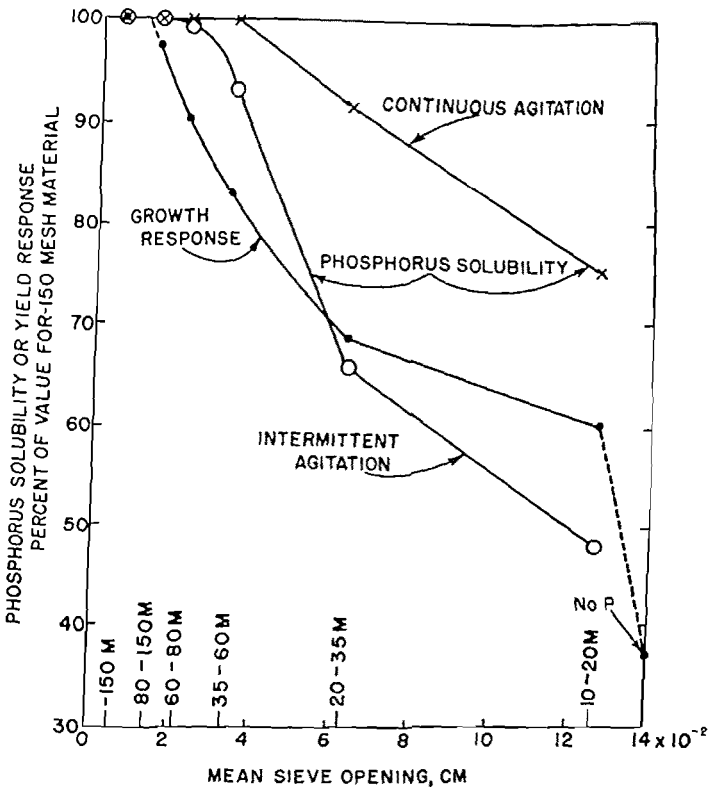


FIG. 11. Influence of particle size of calcium metaphosphate glass on neutral citrate solubility of phosphorus by two procedures and on yield response of millet grown on Evesboro sandy loam soil in greenhouse. Results of Jacob *et al.* (1951) for 25 lb. of total P_2O_5 per acre mixed with upper third of soil; growth period 52 days; L.S.D. (19:1) 3.3 g. per pot.

condition seems to indicate an over-rating of the coarse material by the procedure in which continuous agitation is used in the citrate digestion.

4. Phosphate Rock

In fertilizer parlance, particularly in discussions of processed phosphates, phosphate rock is loosely classified as a citrate-insoluble phosphate. This custom grew out of the circumstance that the insoluble fraction of the phosphorus constitutes a measure of the efficiency of the process as a means for converting rock phosphorus to more soluble forms. Hence, citrate-insoluble phosphorus is identified with unreacted rock in a number of processes. Thus, classification of the slightly soluble phosphates as citrate-insoluble is based on technological association only.

Although the nutrient value of phosphate rock has been studied in

many quarters, systematic studies that permit comparison of solubility with nutrient value are not plentiful. One type of experiment is illustrated by the work of Martin *et al.* (1953), who compared Idaho phosphate rock with superphosphate and ammoniated superphosphate on acid and calareous soils (Figs. 7 and 8). Yield response was not obtained on the calcareous soils. A significant response was shown on acid soils, though it was very low in comparison with that found for superphosphate. It should be noted that the citrate solubility of this particular rock was 1.3 per cent of the total phosphorus, which is exceptionally low for Idaho rock.

Comparison of phosphate rocks has more interest at the moment than the comparison of rock with solubilized phosphates. To this end results for phosphorus solubility and nutrient value of 15 phosphate rocks are given in Table XI. Examination of the results for citrate solu-

TABLE XI

COMPARISON OF CITRATE AND CITRIC ACID SOLUBILITIES OF PHOSPHORUS IN PHOSPHATE ROCK WITH ITS NUTRIENT VALUE AS DETERMINED BY YIELDS OF MILLET IN THE GREENHOUSE[a]

Type and source of phosphate rock[b]	*Total* P_2O_5, *per cent*[c]	*Solubility of* P_2O_5, *per cent of total* P_2O_5		*Relative weight of millet plants*[f]
		Citrate[d]	*Citric acid*[e]	
South Carolina land-rock, Johns Island	26.9	17	29	78
Curaçao Island	40.7	14	36	60
Christmas Island, Indian Ocean	40.0	13	33	57
Morocco, French	33.5	13	31	56
Nauru Island	38.9	10	26	45
Florida waste-pond,[g] Dunnellon	23.6	9	32	45
Florida land-pebble, Mulberry	35.4	9	19	42
Florida land-pebble, Brewster	31.3	8	21	45
Florida hard-rock, Dunnellon	36.0	8	20	45
Idaho, Conda	32.4	7	20	43
Tennessee brown-rock, Mount Pleasant	34.4	6	18	44
Wyoming, Cokeville	30.2	6	14	43
Tennessee blue-rock, Gordonsburg	31.0	5	22	42
Tennessee brown-rock, Wales	34.4	5	17	42
Montana, Garrison	36.4	5	15	43

[a] Brown and Jacob (1945).

[b] All samples were ground to pass the 100-mesh sieve.

[c] Moisture-free basis.

[d] Neutral ammonium citrate.

[e] 2 per cent citric acid.

[f] Yield with superphosphate = 100. All phospbates were used at the rate of 240 pounds of total P_2O_5 per acre of Norfolk loamy fine sand soil (pH 5.5). Relative yield without phosphate addition was 40.

[g] Colloidal phosphate.

bility and yield response suggests a logical division of the materials into two groups on the basis of citrate solubility—one comprising the solubility range above 10, the other the range 10 and below. Citric acid solubilities show greater variability. The group of materials characterized by the higher solubility range consists of four rocks and, interestingly enough, includes Curaçao phosphate and Morocco rock, both recognized as being superior to Florida land pebble and most other rocks for direct application to the soil. This observation points to the possibility that the most promising phosphate rocks for direct application can be selected on the basis of their citrate solubility. Accordingly, South Carolina rock, which is not now mined, may well be the best domestic rock for direct use on the soil.

V. Bases for Guarantee and Quality Control of Fertilizer Phosphorus in Several Countries

Most countries in which commercial fertilizer is used extensively have regulations governing the trade that prescribe the standards of quality of the marketed fertilizer. The standard of quality is maintained by requiring that certain specifications of the product, determined in the laboratory, be guaranteed by the producer. The bases of the guarantee, and hence the analytical method, vary both with and within the class of material from country to country. Consequently, guaranteed specifications based on total phosphorus and soluble phosphorus determined with the use of water, citrate solutions, and citric acid solutions, either singly or in a few selected combinations, are required for one or another phosphate material.

The bases for guarantee and quality control of phosphorus in fertilizer materials and mixtures in 21 countries are indicated in Table XII. At the time of this survey (July 1952), revision of regulations were in progress or under consideration in certain countries. In Norway and Denmark the guarantee must be expressed in terms of elemental phosphorus (P), but in the latter country the equivalent content of P_2O_5 may be stated also. In the other countries the guarantee is expressed in terms of P_2O_5 only.

Australia requires guarantees for total phosphorus in all materials and mixtures, as well as guarantees for phosphorus soluble in water and in either neutral ammonium citrate solution or 2 per cent citric acid (New South Wales). A guarantee of total phosphorus is not required for any fertilizer in Belgium, China (Taiwan), Denmark, Ireland, and New Zealand. In most of the other countries this guarantee is required for only a few products, principally basic slag, bonemeal, guano, and raw mineral phosphates for direct application to the soil. In Japan and

TABLE XII

BASES FOR GUARANTEE AND QUALITY CONTROL OF FERTILIZER PHOSPHORUS IN SEVERAL COUNTRIES[a]

Country	Total phosphorus	Phosphorus soluble in —			
		Water	Ammonium citrate solution[b]		2 per cent citric acid
			Neutral	Alkaline	
United States	Bm, R		F[d]		
Canada	F		F[e]		
Chile	Bm, G, R		Fm, S, Tp		
Brazil, São Paulo	R, S	S	Fm, S		Bm, Bs, G, R
Australia:					
New South Wales	F	F			Fm, R
Queensland, Victoria, South Australia, Western Australia	F	F	F		F
New Zealand	Bm, Bs, Fm, G, R, S, S + R	F[f]			F[f]
Union of South Africa		S, S + R		A, Fc, Fm, S	A, Bs, Fm, R, S, S + R, Sb
China, Taiwan	Bm, Fm,[h] R	A, S[i]		Np, S[i]	Bm, Bs, Pp, Ps
Japan		A, Fc, Fm, K, S		Fc, Fm, Mp, Pp, R, Tp	Bs, Fm,[j] Pp, Ps, R, Sa
Belgium	Bm, Bs, R	S		Bs, Fc	Bs, Fm[k]
Denmark	Bm, R, S	A, K		Fc, Fm, Pp, S, Tp	
France		Sa, Fm[l]		Fm,[m] Np, Pp, S, Tp	Bs
Germany, Federal Republic	Bs, R	F[n]			Bs, Fm[l]
Ireland	Bm, R		Fm, G, S		F[n]
Italy	Bm, G, R	(A, Fc, Fm, Np, Sa),[o] S	(A, Fc, Fm, Np, Sa),[o] Pp, Tp[p]		Bs, Pp, R
Netherlands	Bm, Bs, R	Fm,[m] S		[q]	Bs
Norway	R	A, Fm,[r] S		Np,[r] Pp	Bs, Np,[r] R
Portugal	Bm, Fm,[u] G, R	Fc, Fm, S		[t]	Bs, Fm[r]
Spain	Bm, Bs, G, Pp, Sb	(Fc, Fm),[s] S		Al, Bm, Fc, Fm, Pp, S	Bs
Switzerland		(Bd, Fc, Fm),[s] S		Pp, Tp[p]	Bs
United Kingdom					Bs[r]

[a] Sources of information: *Association of Official Agricultural Chemists (1950), Organization for European Economic Co-operation (1951, 1952), official publications* of the countries, and private communications with officials in the governments and the fertilizer industry.

The materials are identified as follows: A, ammonium phosphates; Al, aluminum phosphate; Bd, dissolved or vitriolized bones; Bm, bonemeal; Bs, basic slag; F, all fertilizers; Fc, compound fertilizers; Fm, mixed fertilizers; G, guano; K, potassium phosphate; Mp, ammoniated magnesium phosphate; Np, nitric acid–phosphate rock products; Pp, precipitated calcium phosphates; Ps, phosphate rock–magnesium silicate glass; R, raw mineral phosphates for direct application to the soil; S, superphosphates; Sa, ammoniated superphosphates; Sb, basic superphosphate; Tp, products of thermal treatment of mixtures of mineral phosphates and alkali salts.

[b] Includes water-soluble phosphorus.

[c] Guarantee is not required in some states.

[d] Guarantee is not required for Bm and R in some states.

[e] Guarantee is not required for R.

[f] Guarantee of water-insoluble phosphorus is also required.

[g] Permitted but not required.

[h] Only mixed fertilizers containing Bm, and "absorbent" fertilizers wherein peat, bentonite, diatomaceous earth, etc., are used as absorbents. Such mixtures need be guaranteed for total phosphorus only.

[i] And certain chemically processed products wherein inorganic fertilizers or inorganic raw materials are used.

[j] Mixtures containing ordinary inorganic materials.

[k] Only mixtures in which the phosphorus is exclusively in the form of Bs.

[l] Only mixtures containing Sa.

[m] Simple mixtures of S with nitrogen and potash salts.

[n] Guarantee is also required for phosphorus that is neither water-soluble nor citric acid-soluble.

[o] It is permitted to guarantee either water-soluble phosphorus or citrate-soluble phosphorus. If citrate-soluble phosphorus is guaranteed, the content of water-soluble phosphorus may also be stated.

[p] Also the products of treating mineral phosphates by other one-step thermal methods.

[q] Although the neutral citrate procedure has been adopted by the state fertilizer and feed control station and is generally used in practice, the alkaline citrate procedure is the officially prescribed procedure for the products indicated in the preceding column.

[r] Not official. Control stations use either the alkaline citrate procedure, the citric acid procedure, or sometimes both procedures.

[s] Guarantee may be on basis of solubility in either water or citric acid solution.

[t] The alkaline citrate method is official but is seldom used.

[u] Only mixed fertilizers in which the phosphorus is solely in the form of either Bm, Bs, G, R, or meat and bone meal.

[v] Except products in which the phosphorus is solely in the forms indicated in footnote *u*.

[w] Both total and citric acid-soluble phosphorus are usually guaranteed, but the law requires a guarantee for total phosphorus only

Switzerland it is necessary to guarantee only the total phosphorus in certain kinds of mixed fertilizers.

Among the countries listed in Table XII, New Zealand is unique in requiring that only the water-soluble and water-insoluble phosphorus be declared in all phosphate fertilizer materials and mixtures, but an additional declaration of citric acid-soluble phosphorus is optional. Although water-soluble phosphorus is the only basis for guarantee of superphosphates in many of the countries, solubility in neutral ammonium citrate is the criterion for this class of materials and mixed fertilizers in the United States, Canada, and Italy.

Phosphorus quality is officially controlled with the aid of the neutral ammonium citrate method in some countries, including the United States, Canada, Mexico, Chile, Brazil (State of São Paulo), Australia (except New South Wales), and Italy. The alkaline ammonium citrate method is used for certain products in most of the European countries. Both procedures may be used in the Netherlands. Neither citrate method is official for any product in Ireland, New South Wales, New Zealand, Union of South Africa, and the United Kingdom. An acid ammonium citrate method is used in China (Taiwan) as an alternative procedure for precipitated calcium phosphates.

The 2 per cent citric acid method was developed specifically for control of phosphorus quality in basic slag, and it is still applied to this material in most countries. Among the exceptions are the United States, Canada, and Australia (except New South Wales), where the neutral citrate method is used, and Denmark (alkaline citrate method). In the United Kingdom basic slag is commonly guaranteed as to both total and citric acid-soluble phosphorus, but the law requires only that the total phosphorus and the fineness of the slag be stated (Ministry of Agriculture and Fisheries, 1951, p. 50). Other products for which guarantees of citric acid-soluble phosphorus are required in some countries include bonemeal, raw mineral phosphates, guano, precipitated calcium phosphates, materials made by heating mineral phosphates with alkali salts and by other one-step thermal processes, and mixed fertilizers.

References

Adams, J. R., and Ross, W. H. 1938. Report on phosphoric acid. A. Effect of the method of filtering on the determination of water-soluble P_2O_5. B. Variation in citrate-insoluble P_2O_5 with the time interval between the water extraction and citrate digestion. *J. Assoc. Offic. Agr. Chemists* **21**: 268–273.

Allen, H. R., Swift, E., Hays, R., and Kaufman, Z. F. 1952. Direct determination of available phosphoric acid by titration of ammonium phosphomolybdate. *J. Assoc. Offic. Agr. Chemists* **35**: 764–767.

Anonymous. 1871. Ueber die Untersuchungsmethoden der künstlichen Düngemittel. *Landw. Vers. Sta.* **14**: 447–457.

ANONYMOUS. 1873. Die Untersuchung der Superphosphate. *Landw. Vers. Sta.* **16**: 233–236.

ANONYMOUS. 1882. Versammlung behufs Vereinbarung über die Bestimmung der Phosphorsäure in ihren verschiedenen Formen zu Halle a. S. *Landw. Vers. Sta.* **27**: 405–411.

ARMIGER, W. H., ANDERSON, M. S., and JACOB, K. D. 1945. Influence of particle size and rate of application of some of the newer water-insoluble phosphorus carriers upon growth of millet. U. S. Department of Agriculture, Bureau of Plant Industry, Soils, and Agricultural Engineering, unpublished report.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. 1884. Proceedings of the Convention of Agricultural Chemists and First Annual Meeting of the Association of Official Agricultural Chemists at Philadelphia, September 8 and 9, 1884.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. 1885. Methods of analysis of commercial fertilizers. *U. S. Dept. Agr., Div. Chem. Bull.* **7**.

ASSOCIATION OF OFFICIAL AGRICULTURAL CHEMISTS. 1950. Official Methods of Analysis. 7th ed., pp. 8–11, Washington, D. C.

BEHRENS, W. U. 1938. Die Untersuchung der Wirkung der Phosphorsäuredünger nach der Keimpflanzenmethode. *Bodenkunde u. Pflanzenernähr.* **9–10**: 14–19.

BROWN, B. E., and JACOB, K. D. 1945. Greenhouse pot-culture tests on rock phosphates as sources of phosphorus for plants. *Am. Fertilizer* **102**(1): 11–12, 28, 30.

BROWN, B. E., REID, F. R., and JACOB, K. D. 1934. Fertilizer value of phosphate rock improved by treatment with water vapor at high temperatures. *Am. Fertilizer* **81**(13): 5–7, 27.

DREYSPRING, C., KRÜGEL, C., and PANTKE, R. 1929. Experiments carried out at the Hamburg-Horn experimental station. VI. Root-solubility of phosphoric acid contained in superphosphate, neutral phosphate, reform phosphate and Algiers phosphate. *Superphosphate* **2**: 61–69, 81–89.

EISENBERGER, S., LEHRMAN, A., and TURNER, W. D. 1940. The basic calcium phosphates and related systems: some theoretical and practical aspects. *Chem. Revs.* **26**: 257–296.

FRESENIUS, R. 1868. Zur Analyse der Superphosphate. *Z. anal. Chem.* **7**: 304–309.

FRESENIUS, R., NEUBAUER, C., and LUCK, E. 1871. Gutachten über die besten Methoden der Analyse der künstlichen Dünger. *Z. anal. Chem.* **10**: 133–158.

GEE, A., and DIETZ, V. R. 1952. Private communication. U. S. Department of Commerce, National Bureau of Standards.

GERLACH, M., and PASSON, M. 1896. Die Bestimmung der leichtlöslichen Phosphorsäure in Thomasmehlen. *Chem. Ztg.* **20**: 87–88.

GUITTONNEAU, G. 1929. Sur l'application des besoins des sols en éléments fertilisants par les culteurs spontanées d'azotobacteur: application aux terres à prunier de l'Agenais. *Compt. rend. acad. agr. France* **15**: 83–88.

HACKL, H. 1921. Über die citratlösliche Phosphorsäure. *Chem. Ztg.* **45**: 730–731.

HARDESTY, J. O., ROSS, W. H., and ADAMS, J. R. 1943. Report on phosphoric acid: factors affecting the availability of ammoniated superphosphates. *J. Assoc. Offic. Agr. Chemists* **26**: 203–211.

HASKINS, H. D. 1920. The effect of mass and degree of fineness on the percentage of available phosphoric acid in precipitated phosphate. *J. Assoc. Offic. Agr. Chemists* **4**: 64–66.

HASKINS, H. D. 1921. Report on available phosphoric acid in precipitated phosphates. *J. Assoc. Offic. Agr. Chemists* **5**: 97–102.

HASKINS, H. D. 1922. Report on precipitated phosphates. *J. Assoc. Offic. Agr. Chemists* **5**: 460–464.

HASKINS, H. D., BIZZELL, J. A., ELLETT, W. B., HARTWELL, B. L., and WILLIAMS, C. B. 1923. Report of committee on vegetation tests on the availability of phosphoric acid in basic slag. *J. Assoc. Offic. Agr. Chemists* **6**: 254.

HASKINS, H. D., BIZZELL, J. A., ELLETT, W. B., HARTWELL, B. L., and WILLIAMS, C. B. 1924. Final report of the special committee of the Association of Official Agricultural Chemists on the availability of phosphoric acid in basic slag phosphates. *J. Assoc. Offic. Agr. Chemists* **7**: 218–252.

HECHT, W. J., JR., WORTHINGTON, E. A., and CRITTENDEN, E. D. 1952. Citrate-insoluble residue from an ammoniated superphosphate: x-ray diffraction study. *Ind. Eng. Chem.* **44**: 1119–1123.

HENDRICKS, S. B., and HILL, W. L. 1950. The nature of bone and phosphate rock. *Proc. Natl. Acad. Sci. U. S.* **36**: 731–737.

HILL, W. L. 1947. Other new phosphates. *Assoc. Am. Fertilizer Control Officials, Offic. Publ.* 1947: 10 pp.

HILL, W. L. 1951. Particle size–plant nutrient relationships in phosphate fertilizers. U. S. Department of Agriculture Bureau of Plant Industry, Soils, and Agricultural Engineering. Presented at the 16th Annual Meeting of the Soil Science Society of America, State College, Pa., Aug. 27, 1951.

HOWES, C. C., and JACOBS, C. B. 1931. Should a change be made in analytical procedure for evaluating available phosphoric acid content of fertilizer materials? *Ind. Eng. Chem., Anal. Ed.* **3**: 70–72.

JACOB, K. D., ARMIGER, W. H., CARO, J. H., and HOFFMAN, W. M. 1951. Report on phosphoric acid: relation of particle size of calcium metaphosphate to its citrate solubility and fertilizer efficiency. *J. Assoc. Offic. Agr. Chemists* **34**: 624–640.

JACOB, K. D., BEESON, K. C., RADER, L. F., JR., and ROSS, W. H. 1931. The solubility of phosphates in neutral ammonium citrate solution. *J. Assoc. Offic. Agr. Chemists* **14**: 263–283.

JACOB, K. D., MAGNESS, R. M., and WHITTAKER, C. W. 1950. Report on phosphoric acid in fertilizers: comparison of neutral ammonium citrate and two per cent citric acid solutions as solvents for alpha phosphate and phosphate rock–magnesium silicate glass. *J. Assoc. Offic. Agr. Chemists* **33**: 234–260.

JACOB, K. D., RADER, L. F., JR., MARSHALL, H. L., and BEESON, K. C. 1932a. Citrate-insoluble phosphoric acid in di- and tricalcium phophates: some factors affecting its determination. *Ind. Eng. Chem., Anal. Ed.* **4**: 25–31.

JACOB, K. D., RADER, L. F., JR., and ROSS, W. H. 1932b. Comparison of two per cent citric acid and neutral ammonium citrate solutions as solvents for phosphates. *J. Assoc. Offic. Agr. Chemists* **15**: 146–162.

JACOB, K. D., RADER, L. F., JR., and TREMEARNE, T. H. 1936. Factors affecting the determination of available phosphorus in calcined phosphate and other water-insoluble phosphates. *J. Assoc. Offic. Agr. Chemists* **19**: 449–472.

JACOB, K. D., RADER, L. F., JR., and WHITTAKER, C. W. 1948. Report on phosphoric acid. A. Effect of continuous agitation during citrate digestion on determination of citrate-insoluble P_2O_5. B. Effect of sulfate on determination of P_2O_5 by the volumetric method. *J. Assoc. Offic. Agr. Chemists*, **31**: 209–234.

JACOB, K. D., and TREMEARNE, T. H. 1937. Effect or removing water-soluble compounds prior to determination of citrate-insoluble phosphorus in fertilizers. *J. Assoc. Offic. Agr. Chemists* **20**: 277–287.

JACOB, K. D., WARD,, F. N., HILL, W. L., and PINKERTON, C. 1947. Report on phosphoric acid: neutral ammonium citrate and two per cent citric acid solutions as solvents for alpha phosphate. *J. Assoc. Offic. Agr. Chemists* **30**: 529–548.

JACOB, K. D., WARD, F. N., MAGNESS, R. M., and WHITTAKER, C. W. 1949. Report on phosphoric acid in fertilizers: comparison of neutral ammonium citrate and two per cent citric acid solutions as solvents for basic slag. *J. Assoc. Offic. Agr. Chemists* **32**: 202–228.

JOSHI, N. V., and AYYAR, C. S. R. 1934. The Azotobacter plaque test of soil deficiency as applied to some Indian soils. *Indian J. Agr. Sci.* **4**: 166–175.

JOULIE, H. 1873. Étude sur le dosage de l'acid phosphorique dans tous les produits qui intéressent l'agriculture et la physiologie: de l'assimilabilité des superphosphates et de sa mesure. *Monit. sci.* (3)**3**: 563–584.

KEENEN, F. G. 1930. Reactions occurring during the ammoniation of superphosphate. *Ind. Eng. Chem.* **22**: 1378–1382.

KENNEN, F. G. 1932. Available phosphoric acid content of ammoniated superphosphate. *Ind. Eng. Chem.* **24**: 44–49.

LEIHRECKE, H. 1935. Nyare rön vid uppslutning av råfosfat med. svavelsyra. *Tek. Tidskr. Uppl. C. Kemi och Bergsvetenskap* **65**: 81–85, 92–94.

LOGAN, M. A., and TAYLOR, H. L. 1938. Solubility of bone salt. III. Partial solution of bone and carbonate-containing calcium phosphate precipitates. *J. Biol. Chem.* **125**: 391–397.

LORAH, J. R., TARTAR, H. V., and WOOD, L. 1929. A basic phosphate of calcium and of strontium and the adsorption of calcium hydroxide by basic calcium phosphate and by tricalcium phosphate. *J. Am. Chem. Soc.* **51**: 1097–1106.

MCGEORGE, W. T. 1939. Factors influencing the availbility of native soil phosphate and phosphate fertilizers in Arizona soils. *Arizona Agr. Expt. Sta. Tech. Bull.* **82**: 295–331.

MACINTIRE, W. H., and HARDIN, L. J. 1935. A modified technic for the determination of citrate-insoluble P_2O_5. *J. Assoc. Offic. Agr. Chemists* **18**: 297–301.

MACINTIRE, W. H., JONES, R. M., and HARDIN, L. J. 1935. Comparison of filtration by gravity and by suction in washing to remove water-soluble P_2O_5 from analytical charges. *J. Assoc. Offic. Agr. Chemists* **18**: 301–306.

MACINTIRE, W. H., MARSHALL, H. L., and MEYER, T. A. 1944. An innovation in the technic of citrate digestions. *J. Assoc. Offic. Agr. Chemists* **27**: 272–283.

MACINTIRE, W. H., SHAW, W. M., and HARDIN, L. J. 1938. Direct determination of available P_2O_5 content of fertilizer. *J. Assoc. Offic. Agr. Chemists* **21**: 113–121; *Ind. Eng. Chem., Anal. Ed.* **10**: 143–152.

MARTIN, W. E., VLAMIS, J., and QUICK, J. 1953. Effect of ammoniation upon the availability of phosphorus in superphosphates as indicated by plant response. *Soil Sci.* **75**: 41–49.

MEHLICH, A. 1937. Use of *Cunninghamella blakesleeana* and *Aspergillus niger* for measuring the manurial requirements of plants. *Soil Sci. Amer. Proc.* **2**: 279–288.

MINISTRY OF AGRICULTURE AND FISHERIES (UNITED KINGDOM). 1951. Manures and fertilisers. *Bull.* **36**.

MOHR, C. 1884. Ueber die quantitative Bestimmung der zurückgegangenen Phosphorsäure und der Phosphorsäure im Dicalciumphosphat. *Z. anal. Chem.* **23**: 487–491.

MOOERS, C. A. 1938. An evaluation of the Cunninghamella and *Aspergillus niger* methods for the determination of the fertilizer needs of a soil. *Soil Sci.* **46**: 211–227.

NEUBAUER, H., and SCHNEIDER, W. 1923. Die Nährstoffaufnahme der Keimpflanzen und ihre Anwendung auf die Bestimmung des Nährstoffgehalts der Böden. *Z. Pflanzenernähr. Düng. u. Bodenk.* **2A**: 329–341.

NIKLAS, H., SCHARRER, K., and STROBEL, A. 1926. Phosphatlöslichkeit und Azotobakterwachstum. *Landw. Jahrb.* **63**: 387–410

OLSEN, S. R. 1952. Measurement of surface phosphate on hydroxylapatite and phosphate rock with radiophosphorus. *J. Phys. Chem.* **56**: 630–632.

ORGANIZATION FOR EUROPEAN ECONOMIC CO-OPERATION. 1951. Fertilisers: Trade Regulations in OEEC Countries. Paris.

ORGANIZATION FOR EUROPEAN ECONOMIC CO-OPERATION. 1952. Fertilisers: Methods of Analysis Used in OEEC Countries. Paris.

PETERMANN, A. 1880. Ueber den landwirthschaftlichen Werth der sogenannten zurückgegangenen Phosphorsäure. *Landw. Vers. Sta.* **24**: 310–350.

RADER, L. F., JR., and ROSS, W. H. 1941. Comparison of the official and MacIntire-Shaw-Hardin methods for determining available phosphoric acid in fertilizer mixtures containing phosphate rock supplements. *J. Assoc. Offic. Agr. Chemists* **24**: 493–498.

RAUSCHER, R. 1927. Über die Anwendbarkeit der Methode Neubauer zur Bestimmung der Löslichkeit der Phosphorsäure in Rohphosphaten. *Fortschr. Landw.* **2**: 85–88.

REYNOLDS, D. S., JACOB, K. D., MARSHALL, H. L., and RADER, L. F., JR. 1935. Phosphate fertilizers by calcination process: factors affecting the reaction between water vapor and Florida land-pebble phosphate. *Ind. Eng. Chem.* **27**: 87–91.

ROSS, W. H., and ADAMS, J. R. 1939. Report on phosphoric acid. A. Effect of method of filtering on determination of water-soluble P_2O_5. B. Variation in citrate-insoluble P_2O_5 with the time interval between water extraction and citrate digesion. *J. Assoc. Offic. Agr. Chemists* **22**: 254–263.

ROSS, W. H., and HARDESTY, J. O. 1936. Report on phosphoric acid: the filtration of citrate-insoluble residues. *J. Assoc. Offic. Agr. Chemists* **19**: 269–279.

ROSS, W. H., and JACOB, K. D. 1931. Report on phosphoric acid: availability of reverted phosphoric acid in ammoniated superphosphates. *J. Assoc. Offic. Agr. Chemists* **14**: 182–196.

ROSS, W. H., and JACOB, K. D. 1937. Report on phosphoric acid: availability of calcined phosphate and other new phosphatic materials as determined by chemical and vegetative tests. *J. Assoc. Offic. Agr. Chemists* **20**: 231–249.

ROSS, W. H., JACOB, K. D., and BERSON, K. C. 1932. Report on phosphoric acid: composition and fertilizer efficiency of the insoluble phosphates in ammoniated superphosphates. *J. Assoc. Offic. Agr. Chemists* **15**: 227–266.

ROSS, W. H., and MERZ, A. R. 1931. Phosphoric acid. *In* Wiley's Principles and Practice of Agricultural Analysis. 3rd ed., Vol. II, Fertilizers and Insecticides. pp. 41–212, Chemical Publishing Co., Easton, Pa.

ROSS, W. H., and RADER, L. F., JR. 1940. Report on phosphoric acid: a comparison of the official and MacIntire-Shaw-Hardin methods for determining available phosphoric acid. *J. Assoc. Offic. Agr. Chemists* **23**: 234–242.

SACKETT, W. G., and STEWART, L. C. 1931. Bacteriological method for determining mineral soil deficiencies by use of soil plaque. *Colorado Agr. Expt. Bull.* **375**: 3–36.

SCHARRER, K., and SCHREIBER, R. 1940. Neubauer-Untersuchungen über die Aufnahme der Phosphorsäure verschiedener Phosphorsäuredüngemittel. *Bokenkunde u. Pflanzenernähr.* **18**: 376–388.

STOHMANN, F. 1864. Ueber die Untersuchungmethoden der käuflichen Düngstoffe. *Z. anal. Chem.* **3**: 184–199.

STROBEL, A., and SCHARRER, K. 1926. Versuche über die biochemische Ausnützung der verschiedenen Phosphorsäureformen. *Z. angew. Chem.* **39**: 1579–1584.

THORNTON, S. F. 1931. The Neubauer method as applied to the determination of the availability of phosphate materials. *J. Assoc. Offic. Agr. Chemists* **14**: 292–295.

THORNTON, S. F. 1932. Factors affecting the availability of phosphate fertilizers as shown by the Neubauer method. *J. Assoc. Offic. Agr. Chemists* **15**: 163–166.

THORNTON, S. F. 1935. Soil and fertilizer studies by means of the Neubauer method. *Indiana Agr. Expt. Sta. Bull.* **399**.

THUN, R. 1939. Über das Wirkungsverhältnis verschiedener neuerer Phosphorsäuredünger zu den bisher gebräuchlichen Düngerformen. *Bodenkunde u. Pflanzenernähr.* **14**: 112–132.

TRUFFAUT, G., and BEZSSONOFF, N. 1927. Mesure de l'assimilabilité de divers phosphates par leur action sur la fixation bactérienne de l'azote. *Compt. rend.* **185**: 85–86.

WAGNER, P. 1886. Vereinbarungen zwischen süddeutschen Versuchsstationen und Düngerfirmen über eine neue Grundlage zur Feststellung des Handelswerthes der Superphosphate und präcipitirten Phosphate. *Chem. Ztg.* **10**: 1–2, 19, 37.

WAGNER, P. 1894. Die Bestimmung der citratlöslichen Phosphorsäure in Thomasschlacken und unaufgeschlossenen mineralischen Phosphaten. *Chem. Ztg.* **18**: 1153–1154.

WAGNER, P. 1895. Die Bestimmung der citratlöslichen Phosphorsäure in Thomasmehlen. *Chem. Ztg.* **19**: 1419–1421.

WAGNER, P. 1899. Die Bestimmung der wirksamen Phosphorsäure in Thomasmehlen mit 2% iger Citronensäurelösung. *Landw. Vers. Sta.* **52**: 10–25.

WAGNER, P., DORSCH, R., ASCHOFF, F., and KUNZE, R. 1903. Die Bestimmung der zitronensäurelöslichen Phosphorsäure in Thomasmehlen. *Mitt. Verein. Deut. Landw. Vers. Sta.* **1**.

WHITE, L. M., HARDESTY, J. O., and ROSS, W. H. 1935. Ammoniation of double superphosphate. *Ind. Eng. Chem.* **27**: 562–567.

WILHELMJ, A., KARST, H., and GERICKE, S. 1929. Über die Bedeutung der Ammonzitratlöslichkeit im Thomasmehl und im Rhenaniaphosphat. *Z. Pflanzenernähr. Düng. u. Bodenk.* **14A**: 42–61.

CHAPTER XI

Domestic Phosphate Deposits

V. E. McKELVEY, J. B. CATHCART, Z. S. ALTSCHULER, R. W. SWANSON, and KATHARINE L. BUCK

I. Introduction

Phosphorus has been called the "bottleneck of the world's hunger" (Rorty, 1946). This is true for large parts of the world, particularly Asia, but the United States, fortunately, has large reserves of mineral phosphate available to replace the phosphate removed from the soil by crops and erosion. The chief purpose of this account of the characteristics, distribution, and reserves of domestic phosphate deposits is to provide a background for the consideration of problems of phosphorus in relation to fertilizer and crop production; in addition, the authors wish to show that increased domestic consumption of phosphorus fertilizer need not be limited by lack of phosphate reserves in the United States.

II. Principal Types of Phosphate Deposits

Phosphorus makes up about 0.12 per cent of the earth's crust—it is the eleventh most abundant element. It forms complex compounds with a wide variety of metals—more than 150 minerals are known that contain 1 per cent or more P_2O_5. Most of the phosphorus in the earth's crust, however, is found in one mineral family, the apatite group, $Ca_{10}(PO_4, CO_3)_6(F, Cl, OH)_2$. Because of its essential content of an anionic radicle, the PO_4 tetrahedron, as well as of a simple anion, usually fluorine, and a simple cation, usually calcium, apatite serves as a host for a great many minor substitutions. Thus, small amounts of VO_4, AsO_4, SiO_4, SO_4, and CO_3 or CO_4 may be present in place of equivalent amounts of PO_4. The fluorine position may be occupied completely or in part by F, Cl, or OH. In addition, minor amounts of Mg, Mn, Sr, Pb, Na, U, Ce, Y, and other rare earths may substitute for calcium. The variety of structural elements in apatite enhances the number of substitutions which occur, as cationic replacements involving loss or gain of valence may be compensated for by anionic replacements of opposite nature. These facts account in great measure for the rich suite of minor metals found in many

TABLE I

CHARACTERISTICS OF PRINCIPAL TYPES OF PHOSPHATE DEPOSITS

Type (and examples)	*Origin*	*Associated rocks*	*Shape and structure of deposits*	*Principal phosphate minerals*	*Common minor metals*	*Range of reserves in individual fields, tons of rock*
1. Igneous apatites						
a. Apatite intrusions (Kola peninsula, USSR; Eastern Uganda; Palabora, East Transvaal)	Differentiation from cooling basic magma	Nepheline syenite, ijolite, carbonatite pyroxenite, magnetite	Inclined sheets, in some places interleaved with other rocks around a circular core	Fluorapatite ($Ca_{10}(PO_4)_6F_2$)	Sr, rare earths	10^9–10^{10}
b. Apatite marginal differentiations (Eastern Adirondacks)	Metasomatic differentiation along contacts of alaskite intrusions	Alaskite, magnetite	Steeply inclined irregular masses	Fluorapatite	[a]	10^3–10^6
c. Apatite pegmatite (Southern Ontario)	Late stage differentiation from cooling basic magma	Pyroxenite, syenite, calcite, phlogopite, titanite	Steeply inclined tabular masses	Fluorapatite	Sr, rare earths, As	10^3–10^5
d. Hydrothermal veins, disseminations and replacements (Norwegian apatite veins, Virginia nelsonite)	Late stage emanation from basic magma, generally cutting or partly replacing earlier differentiates	Ilmenite, nelsonite, anorthosite	Steeply inclined tabular masses or irregular disseminated bodies	Fluorapatite; Chlorapatite ($Ca_{10}(PO_4)_6Cl_2$); Hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$)	[b]	10^4–10^7
2. Marine phosphorites	Organic or inorganic precipitation on margins of oceanic basins	Carbonaceous mudstone, chert	Widespread blanket, folded to varying degree	Carbonate-fluorapatite ($Ca_{10}(PO_4,CO_3)_6F_{2-3}$)	V, Cr, rare earths, Co, Ni, Mo, U, Zn, Ag, As, Cd, Cu, Tm, Be	10^9–10^{11}
a. Geosynclinal phosphorites (Western U. S.; North Africa; Kara Tau U.S.S.R.)						
b. Platform phosphorites (Cretaceous glauconite marls of Gulf Coastal Plain; Tennessee "blue-rock"; eastern part of the western field)	Organic or inorganic precipitation in epicontinental seas; often reworked from older phosphatic formations	Limestone, dolomite, quartz, sandstone, glauconite, carbonaceous mudstone	Widespread blanket, locally moderately warped	Carbonate-fluorapatite	V, Cr, rare earths, Co, Ni, Mo, U, Zn, Ag, As, Cd, Cu, Tm, Be	10^6–10^{10}

3. Residual phosphorite (Tennessee brown-rock deposits)	Insoluble residuum remaining after decomposition of phosphatic limestone in humid climate	Limestone, clay, quartz sand	Near-surface blanket lying on irregular etched bed-rock surface	Carbonate-fluorapatite	As, U	10^4–10^5
4. River pebble (Florida, South Carolina river-pebble fields)	Fluvial transport of weathered-out phosphorite particles in humid or subtropical regions of low relief	Quartz sand	River bars, channel fillings and terraces	Carbonate-fluorapatite	[b]	10^4–10^7
5. *Phosphatized rock*						
a. Calcareous terrane (Florida hard-rock Tennessee white-rock, Nauru and Ocean Islands)	Replacement of limestone or clay in tropical or sub-tropical climate by phosphate derived from overlying phosphatic rocks or guano	Limestone, dolomite, clay, quartz sand	Near-surface irregular blanket	Carbonate-hydroxyl-fluorapatite ($Ca_{10}(PO_4,CO_3)_6(OH,F)_{2-3}$); Hydroxylapatite ($Ca_{10}(PO_4)_6(OH)_2$); Whitlockite ($\beta$-$Ca_3(PO_4)_2$); Brushite ($HCaPO_4{\cdot}2H_2O$); Monetite ($HCaPO_4$); Wavellite ($Al_3(OH)_3(PO_4)_2{\cdot}5H_2O$); Pseudowavellite ($CaAl_6(PO_4)_4(OH)_5{\cdot}H_2O$); Taranakite ($K_2Al_6(PO_4)_6(OH)_2{\cdot}18H_2O$);	Zn, Ag, Cd, Ga	10^4–10^7
b. Igneous terrane (Daito Jima, Malpelo, Grand Connetable islands)	Replacement of igneous rock or clay by phosphate derived from guano	Trachyte, andesite, basalt, granite, gabbro	Near-surface irregular blanket	((Al,Fe)$PO_4{\cdot}2H_2O$). High Al member occurs in acid igneous rocks, high Fe member in intermediate and basic rocks Orthorhombic series: Variscite ($AlPO_4{\cdot}2H_2O$); Barrandite ((Al,Fe)$PO_4{\cdot}2H_2O$); Strengite ($FePO_4{\cdot}2H_2O$); Monoclinic series: Metavariscite Clinobarrandite Metastrengite	[b]	10^4–10^5
6. Guano (islands along Peruvian and Chilean coasts)	Accumulation of sea fowl or bat excreta	All varieties (no genetic relationship)	Surficial irregular blanket	Carbonate-hydroxylapatite Hydroxylapatite Whitlockite Brushite Monetite	[b]	10^4–10^6

[a] Metals listed are those present in amounts greater than 5 times their average concentration in the earth's crust, exclusive of detrital impurities.
[b] No information available.

apatite deposits and so important in the agricultural use of phosphate rock.

In nature phosphate is concentrated by igneous, sedimentary, weathering, and biologic processes. The geology of the important producing types of deposits is treated here to promote greater understanding of the potentialities of these deposits in this country. They are six in number, namely apatite deposits of igneous origin, marine phosphorites, residual phosphorites, river-pebble deposits, phosphatized rock, and guano (Table I).

1. Apatite Deposits of Igneous Origin

Apatite deposits of igneous origin are found as intrusive masses, hydrothermal veins or disseminated replacements, marginal differentiations along or near the boundaries of intrusions, and pegmatites. These deposits are generally associated with bodies of nepheline syenite, ijolite, alaskite, carbonatite, pyroxenite, ilmenite, magnetite, or nelsonite.

The largest of the apatite deposits of igneous origin are intrusive sheets associated with syenite, pyroxenite, or amphibolite, and in some places with carbonatite or magnetite. These sheets are inclined and in some places roughly interleaved around a circular core. The apatite-rich layers range in thickness from tens to hundreds of feet or more and are traceable for hundreds of feet or even a few miles. Their P_2O_5 content is as much as 35 per cent, and reserves are measurable in billions of tons. The higher-grade rock is not beneficiated. Lower-grade rock containing 5 to 25 per cent P_2O_5 may be beneficiated by grinding and sieving or magnetic separation to yield a high-grade apatite concentrate. No attempt is made to beneficiate the very low-grade magnetite-apatite rock for phosphate. On smelting, such rock yields a phosphate-rich slag. No important deposits of this type are known in this country, but three of the largest apatite deposits in the world are of igneous origin, namely the Khibin deposits on the Kola peninsula, U. S. S. R. (Fiveg, 1937); the eastern Uganda deposits (Davies, 1947); and the Palabora deposits in East Transvaal (Shand, 1932). The Kiruna magnetite deposits in Sweden and the Iron Mountain hematite deposits in Missouri (thought to be weathered magnetites) are apatite-rich iron ores of this type (Lindgren, 1933, p. 793).

The vein, disseminated, marginal, and pegmatite deposits are either less extensive or of lower quality, or both, and hence are of less economic importance. Most of the reserves are measurable in thousands rather than millions of tons, and the P_2O_5 content of large masses is generally less than 20 per cent. Examples include the hydrothermal

TABLE II

REPRESENTATIVE ANALYSES OF PRINCIPAL TYPES OF PHOSPHATE DEPOSITS

	A*	B	C	D	E	F	G	H	I	J
CaO	52.85	55.10	52.40	42.30	41.87	50.19	46.35	54.42		
P_2O_5	40.62	41.24	40.98	28.60	30.17	35.33	44.28	38.92	38.75	38.5
Al_2O_3		0.12		1.40	2.72	1.19	0.11	0.30	4.31	5.0[e]
Fe_2O_3	0.29		0.00	0.70	3.43	0.88			33.40	7.4
FeO		0.36	0.21							
MgO	0.01	0.23	0.54	0.60	0.16	0.03	2.17	0.00		
MnO	0.07	0.12	1.52		0.23	0.036			0.08	
Re_2O_3[a]	0.98									
SrO	2.57									
TiO_2				0.10	0.16	0.03			5.42	
Na_2O	1.10		0.00	0.90	0.27	0.42	0.005	0.45		
K_2O	0.21		0.00	0.88	0.64	0.26		tr		
Cr_2O_3					0.003	0.01				
V_2O_3				0.07		0.02				
SiO_2	0.26				14.38	4.32	2.80[e]	0.20	4.11	25.9
ZnO							1.99			
CO_2		0.73		3.30	1.05	2.78	0.02	2.04	0.00	
SO_3				2.80	0.63	0.12	0.73	0.00		
F	3.58	3.65	1.15	2.60	3.24	3.76	0.02	2.62	0.00	
Cl			3.74		0.01					
H_2O+			0.06	0.87			1.61	2.78	14.90	2.30
H_2O-							0.10		3.80	
L.O.I.				4.50[b]	1.75	1.32				
Insol.		0.22		10.50						
	100.75	101.77	100.60	100.12	100.71	100.70				
Less O-F	1.50	1.54	0.49	1.09	1.36	1.58				
Less O-Cl			0.84							
Total[f]	99.25	100.23	99.27	99.03	99.35	99.12	100.23[d]	100.63	99.77	

* A. Igneous apatite intrusion, Kola Peninsula, U.S.S.R. (composite of 110 apatite separates); Volodchenkova, A. I., and Melentiev, B. N., 1938.

B. Apatite pegmatite, Hastings Co., Ontario; Walker, T. L., and Parsons, A. L., 1926.

C. Hydrothermal chlorapatite, Kanawaga Pref., Japan; Harada, Z., 1938.

D. Marine geosynclinal phosphorite, Phosphoria formation, Coal Canyon, Wyoming (Bed 24, sample #2077); unpublished analysis, U. S. Geological Survey.

E. Residual phosphorite, high-grade brown-rock phosphate, Wales, Tennessee; Jacob, K. D. *et al.*, 1933.

F. Phosphatized limestone (hard rock), Dunnellon, Florida, (sample #434); Jacob, K. D. *et al.*, 1933.

G. Phosphatized limestone, beta tricalcium phosphate, Nueva Leon, Mexico; Cady, J. G. *et al.*, 1952.

H. Phosphatized limestone, Nauru Island; Jacob, K. D. *et al.*, 1933.

I. Phosphatized augite-andesite, Malpelo Island; McConnell, D., 1943.

J. Phosphatized trachyte, Clipperton Atoll; Hutchinson, G. E., 1950.

[a] Total rare earths.

[b] Exclusive of CO_2 and H_2O.

[c] Insol. in 1:1 HCl plus SiO_2 liberated by dehydration.

[d] Also present traces of Mn, Cu, V, Sr, Ni, Ba.

[e] Includes insoluble residue.

[f] Totals as corrected in original publication.

apatite-ilmenite (nelsonite) disseminated deposits in Virginia (C. S. Ross, 1941); the apatite veins in Norway (Lindgren, 1933, p. 764); the apatite-magnetite marginal deposits associated with alaskite in the eastern Adirondacks (Lindgren, 1933, p. 794); and the apatite-pegmatite deposits in southern Ontario (Adams and Barlow, 1910).

The apatite that predominates in all of these deposits is fluorapatite; chlorapatite is rare in large deposits. Strontium and the rare earths commonly make up 1 to 3 per cent of the mineral and substitute for calcium in the crystal structure (Table II). Other metals are not abundant.

2. Marine Phosphorites

Marine phosphorites are believed to be inorganically and organically precipitated on shelving margins of large oceanic basins. As cold water rises from the depths along the continental slopes, its pH increases with increase in temperature and with the decrease in partial pressure of CO_2, and phosphate is then precipitated (Kazakov, 1937; and McKelvey *et al.*, 1953). The marine phosphorites may be divided into two principal facies—geosynclinal and platform, the one commonly the stratigraphic equivalent of the other.

The geosynclinal deposits—of which those of western United States (Mansfield, 1927; McKelvey *et al.*, 1953), North Africa (Cayeux, 1941), and the Kara-Tau of the Soviet Union (Vol'fkovich, 1945) are the world's outstanding examples—are associated with chert, black carbonaceous shale, and minor amounts of limestone. The phosphate deposits consist of layers of phosphatic pellets, generally less than 0.1 to 2 mm. in diameter, that were deposited as blankets over thousands of square miles. Many of these layers are 3 feet or more in thickness and contain 25 to 35 per cent P_2O_5. The fluorapatite content in the minable layers of such formations is commonly 3000 to 25,000 kg. per square meter, and the fluorapatite content of the whole formation may be 25,000 to 75,000 kg. per square meter.

Most of the platform deposits are associated with limestone, glauconite sandstone, quartz sandstone, and, less commonly, clay; some are associated with bituminous shales; and a few are associated with manganese- and iron-ore deposits. The glauconitic marls of Alabama and Mississippi (E. A. Smith, 1892; Monroe, 1941) are examples of the first group; the "blue-rock" deposits of Tennessee (Smith and Whitlatch, 1940) of the second; and the manganiferous phosphatic shales of Arkansas (Branner and Newsom, 1902) of the third.

The phosphate in the platform deposits generally occurs as large nodules or pebbles, most of which are 2 to 10 mm. in diameter (but

some of which may be 25 or even 50 mm. in diameter), sparsely disseminated in a matrix of nonphosphatic sediment. Some phosphate is in the form of phosphatized shells or fish remains. In younger, unconsolidated deposits, the phosphatic particles can be segregated from the matrix by washing or flotation. In many platform deposits the P_2O_5 content of the pebbles is only 15 to 25 per cent. The fluorapatite content of such formations generally ranges from 100 to 1500 kg. per square meter but may be as much as 5000 to 10,000 kg. per square meter. The best platform deposits have resulted from submarine reworking of older, less phosphatic formations. They commonly are found as basal conglomerates of formations formed by transgressing seas (Goldman, 1922; Pettijohn, 1926; Kazakov, 1937).

The phosphate mineral in the marine phosphorites is generally carbonate-fluorapatite (Altschuler and Cisney, 1952). Marine phosphorites, particularly the geosynclinal facies, contain a host of minor constituents, some of which are important as byproducts recoverable in the manufacture of fertilizers and chemicals and some of which are essential to plant growth. These trace constituents include vanadium, strontium, nickel, molybdenum, zinc, copper, rare-earths, silver, and uranium (Oertel and Stace, 1947; Robinson, 1948; Jacob *et al.*, 1933; Hill *et al.*, 1932; Hébert, 1947; McKelvey and Nelson, 1950).

Reserves of the marine phosphorites are measurable in millions or billions of tons, mainly accounted for by geosynclinal deposits. With a few exceptions, the platform deposits are not of commercial value at present.

3. *Residual Phosphorites*

Carbonate-fluorapatite is less soluble than calcite, and therefore is residually concentrated during the weathering of marine phosphatic limestones. These residual phosphate deposits are most common in humid climates; those in Tennessee (Smith and Whitlatch, 1940) and Kentucky (Phalen, 1915) are good examples. These deposits resemble the marine phosphorites (from which they are generally derived) in the composition of their phosphatic particles, but they differ in distribution and extent. Most of these deposits are at or near the surface, and they occur on irregular, deeply etched bedrock surfaces. The P_2O_5 content ranges from 15 to 35 per cent or more and the fluorapatite content may be 1000 to 10,000 kg. per square meter.

Reserves of the residual deposits are measured in thousands or at most millions of tons. Some residual phosphorites, those in Tennessee for example, are important producers because of their high quality and thin cover.

4. *River-Pebble Deposits*

Some of the clastic phosphate that is left behind during the weathering of phosphatic limestones is moved by runoff to the streams. In humid regions of low relief, such as Florida (Mansfield, 1942a) and South Carolina (G. S. Rogers, 1915), phosphate nodules commonly make up the only coarse detritus on the stream bottoms. These concentrations are known in the industry as river-pebble deposits and are easily recoverable. Reserves are measurable in millions of tons. Known deposits of this type, however, cannot be mined now in competition with other types because the P_2O_5 content of the nodules is too low (presumably as a result of leaching in the stream), and the deposits are too small and patchy.

5. *Phosphatized Rock*

In regions of subtropical or tropical weathering where decaying vegetation lowers the pH of meteoric waters, the carbonate-fluorapatite in sedimentary rocks is eventually decomposed. Some of it disappears in runoff, but in some places it is reprecipitated after traveling only a short distance, particularly if the phosphatic solutions encounter aluminous or iron-bearing rock or limestone in a different chemical environment. These deposits consist of encrustations on surfaces of joints or cavities, or an irregular, tabular replacement of bedrock or residual boulders. The mineral composition depends upon the lithology of the replaced rock. Phosphatized limestone generally consists of some form of calcium phosphate; whereas iron and aluminum phosphate minerals of the variscite and metavariscite series are common in phosphatized volcanic rocks, and wavellite and pseudowavellite in clays. The P_2O_5 content of these deposits depends on the degree of replacement. Some deposits have 35 per cent or more P_2O_5. Although minor metals are not abundant, gallium may be prominent in wavellite. These deposits are generally of limited extent, and with few exceptions their reserves are measurable in thousands or millions of tons. Examples are the white-rock deposits of Tennessee (Smith and Whitlatch, 1940) and the hard-rock deposits of Florida (Mansfield, 1942a).

The phosphate in the phosphatized rocks of most insular deposits is derived from guano rather than from phosphatic limestone. The deposits of Fais, Angaur, and Kita-daito (Rodgers, 1948) originated in this way.

6. *Guano*

Accumulations of the droppings of sea fowl and bats are rich in nitrogenous materials and phosphates. Leaching or decomposition of

the nitrogenous material of this guano yields a residue rich in phosphate. It is interesting to note that the largest guano accumulations are found in the vicinity of the cold, phosphate-rich waters (Sverdrup *et al.*, 1946, p. 942) from which the marine phosphorites precipitate. The abundant supply of phosphate in these waters nourishes a luxuriant plankton growth, which in turn supports a large fish population on which the sea fowl feed. Conditions most favorable for the accumulation of guano deposits are found along the west coast of the continents in low latitudes where cold waters upwell and where the dry, subtropical climate inhibits destruction of the guano (Hutchinson, 1950, p. 6). Such deposits occur along the west coasts of Lower California, South America, and Africa.

The mineralogy of guano is complex and depends to some extent on the stage of decomposition and leaching. Slightly decomposed deposits contain soluble ammonium and alkali oxalates, sulfates, and nitrates and a variety of magnesium phosphates and ammonium-magnesium phosphates. Largely decomposed guano consists essentially of calcium phosphates.

The guano deposits are limited in extent and their reserves are seldom measured in millions of tons—in fact, most of the rich deposits are already exhausted. The P_2O_5 content of guano is generally less than 20 per cent, but, because the P_2O_5 is readily available and because other nutrients, particularly nitrogen, are present, guano is a valued fertilizer. Minor metals are not abundant in guano.

7. Other Types

Other sources of "mineral" phosphates are bone piles found at ancient salt licks and water holes, glauconite, and phosphatic iron ores that yield a basic slag in the manufacture of steel (Hertzog, 1935). The bone piles are no longer important. Glauconite contains only 1 to 5 per cent P_2O_5, but, as it also contains K_2O, it has had some use as a fertilizer; reserves are measurable in millions and billions of tons. Phosphatic iron ores include marine deposits of the type found in the Clinton formation as well as apatite-rich magnetite deposits of igneous origin. The basic slag (Thomas meal) made from these ores contains 8 per cent or more P_2O_5. Reserves of the phosphatic iron-ore source rocks, which contain only 0.5 to 5 per cent P_2O_5, are measured in millions of tons.

III. Distribution and Geology of Domestic Deposits

All the principal types of phosphate deposits are found in this country, and concentrations of one type or another are found in 30 of the

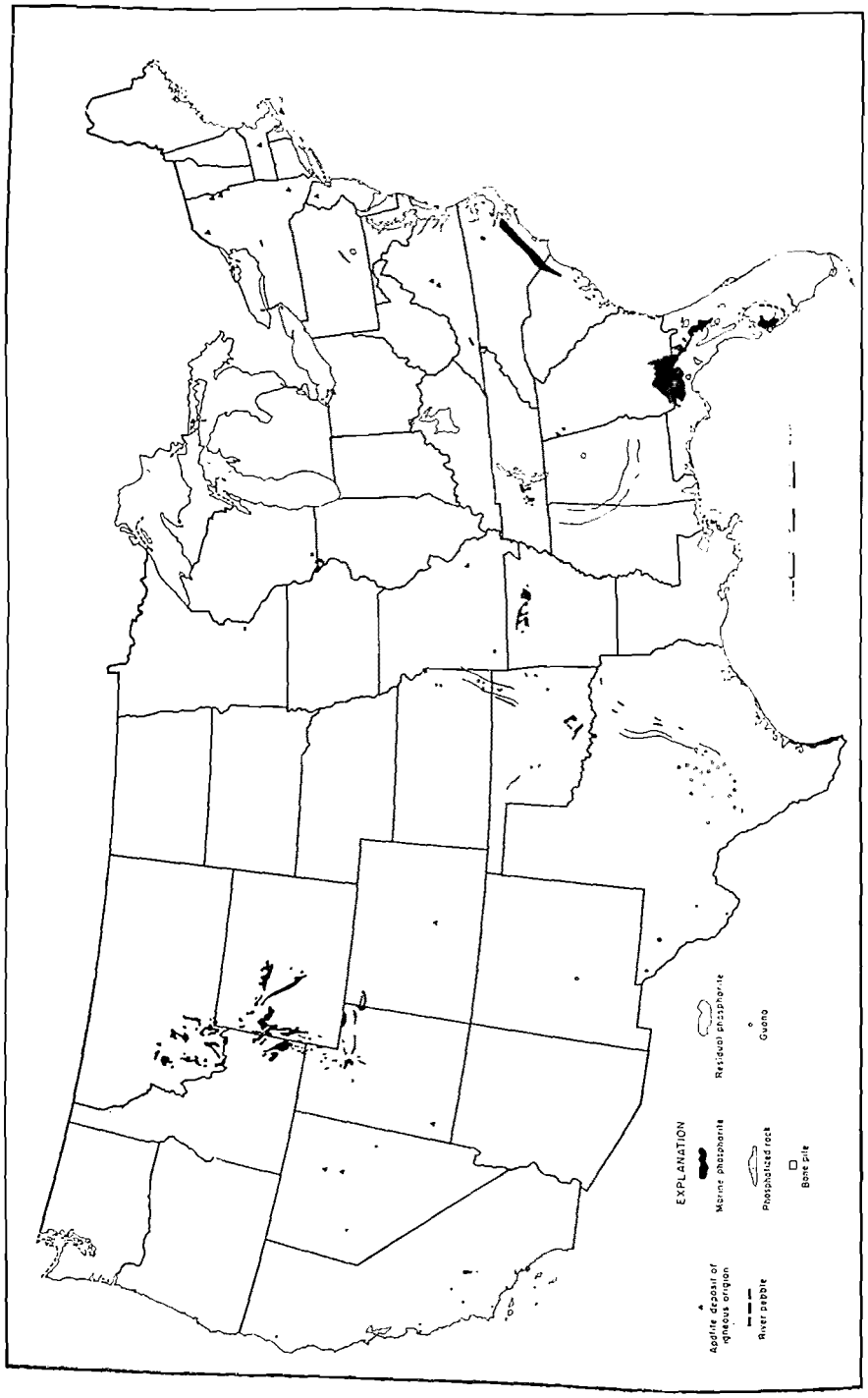


FIG. 1. Distribution of phosphate deposits in the United States. (Only deposits in Montana, Wyoming, Idaho, Utah, Tennessee, and Florida are being mined now or are likely to be of commercial value in the foreseeable future.)

states (Fig. 1). Only about half of these states—Pennsylvania, Virginia, North Carolina, South Carolina, Georgia, Alabama, Florida, Tennessee, Kentucky, Arkansas, Idaho, Wyoming, Utah, and Montana—have ever produced phosphate. Current production of phosphate rock, listed in order of rate of production (Table III), comes from only four fields: the land-pebble field of Florida; the brown-rock field of Tennessee; the western field; and the hard-rock field of Florida. Because future production is likely to be restricted largely to these same fields, we place the chief emphasis on them in our description of domestic deposits.

1. Florida Land-Pebble Field

The Florida land-pebble field has produced about 117 million tons during the period from 1891, when mining began, through 1949 (Table III). In 1949 it produced about 6.7 million tons (Johnson and Tucker, 1951)—slightly more than one-third of the world's production and about three-fourths of our domestic production.

The Florida land-pebble deposits are part of the Bone Valley formation, of probable Pliocene age, which extends over an area of about 2600 square miles, chiefly in Polk and Hillsborough Counties, in the west-central part of the Florida peninsula (Eldridge, 1893; Sellards, 1915; Matson, 1915; Roundy, 1941; Mansfield, 1942a; Cathcart *et al.*, 1953). The Bone Valley formation was deposited on the eroded surface of the underlying phosphatic Hawthorn formation of Miocene age by a transgressing sea that reworked and partly sorted the thick, residual phosphatic mantle found on the Hawthorn at the close of the Miocene. Since its deposition, the upper part of the Bone Valley has been deeply weathered (Fig. 2). Much of the phosphate in this upper leached zone has been removed and some has phosphatized clay. The Bone Valley deposits are thus complex—partly residual, partly marine reworked, and partly phosphatized clay.

All the phosphate recovered from the land-pebble field is in the lower, less weathered part of the Bone Valley formation, called the matrix. The matrix rests on a "bed clay" at the top of the Hawthorn formation which has a karst surface (Fig. 3). The thickness of the matrix ranges from 1 to 50 feet and averages about 12 feet; the thickest deposits are commonly in old sinkholes in the Hawthorn formation.

The matrix consists of an unconsolidated mixture of phosphorite pellets and pebbles, boulders of partly phosphatized limestone, quartz sand, and montmorillonite clay. The matrix typically consists of about one-third phosphorite particles coarser than 0.1 mm., one-third quartz-sand, and one-third clay. Depending partly on the thickness and the

TABLE III

PRODUCTION AND RESOURCES OF PHOSPHATE ROCK IN THE UNITED STATES (TONNAGES ARE IN MILLIONS OF LONG TONS)

	Production		*Inferred reserves minable under present conditions*		*Additional inferred resources minable under changed conditions*	
Source and type	*Marketed product*[a]	P_2O_5 *content*[b]	*Marketable product*	P_2O_5 *content*	*Product*	P_2O_5 *content*
Florida						
Land pebble						
In matrix	124.7[c]	41.7	1,000[d]	330[d]	2,000[d,e]	600[d,e]
In leached zone	.....	.....	.....	.....	800[d,f]	180
River pebble	1.3[g]	0.3	.....	.....	50[h]	12
Hard rock	14.0[i]	4.8	1,040[h,i]	330	500[h,i]	140
Soft rock	1.1	0.2	[k]	[k]	[k]	[k]
Hawthorn formation	.....	.....	.....	.....	20,000[h]	4,000
Total Florida	141.1	47.0	2,040	660	23,350	4,932
South Carolina						
Land rock	9.3[l]	2.5	.....	.....	9[h]	2.4
River rock	4.1[l]	1.0	.....	.....	[m]	[m]
Total South Carolina	13.4	3.5	.....	.....	9	2.4
Tennessee						
Brown rock	31.1[n]	9.0	85[h]	15	[m]	[m]
Blue rock	1.3[n]	0.4	.....	.....	83	25
White rock	0.02	0.007	.....	.....	15	4
Phosphatic limestone	.....	.....	.....	.....	5,300[a]	1,100
Total Tennessee	33.3[o]	10.0[o]	85	15	5,398	1,129
Western field (Phosphoria formation)	6.8	1.9	3,000[p]	870	20,000[q]	5,800
Arkansas	0.03	0.01	.....	.....	20[h]	5
Other states (Ala., Ky., N. C., Pa.)	0.17	0.05	.....	.....	[l]	[l]
Grand total (rounded)	195.00	62.00	5,100	1,500	49,000	12,000

[a] Figures rounded off from those compiled by Jacob (1953) supplemented by figures for 1949 from the Bureau of Mines Mineral Yearbook.

[b] Approximate.

[c] Includes some river pebble and soft rock.

[d] Preliminary figures based upon recent U. S. Geological Survey investigations.

[e] Includes about 1 billion tons in the northern part of the district containing 27-30 per cent P_2O_5. The remainder is in the southern part of the district.

[f] All in the northern part of the field; comprised of: (1) 1.5 billion tons, in deposits more than 5 feet thick, 20 per cent (300 million tons) which is minus 150-mesh in size and contains 15 to 30 per cent P_2O_5 and a similar amount of Al_2O_3; (2) 2.5 billion tons in deposits more than 1 foot thick, 20 per cent (500 million tons) which is minus 150-mesh in size.

[g] Some river pebble is included with land pebble.

[h] Figures rounded off from estimates compiled by Mansfield, 1942b.

[i] Includes some soft rock.

[j] Includes soft rock.

[k] Included with hard rock.

[l] Some river rock included with land rock.

[m] Data not available.

[n] Virginia apatite and some blue-rock included with Tennessee brown-rock.

[o] This figure is higher than the sum of the individual items because separate data for the different types of Tennessee phosphate are not available for the years prior to 1905.

[p] Preliminary, incomplete estimates based upon recent investigations of the U. S. Geological Survey; about one fourth is acid-grade (> 31 per cent P_2O_5) and the remainder is furnace-grade (> 24 per cent P_2O_5).

[q] Preliminary, incomplete estimates based upon recent investigations of the U. S. Geological Survey; rocks are of minable thickness, contain more than 24 per cent P_2O_5, but lie below entry level.

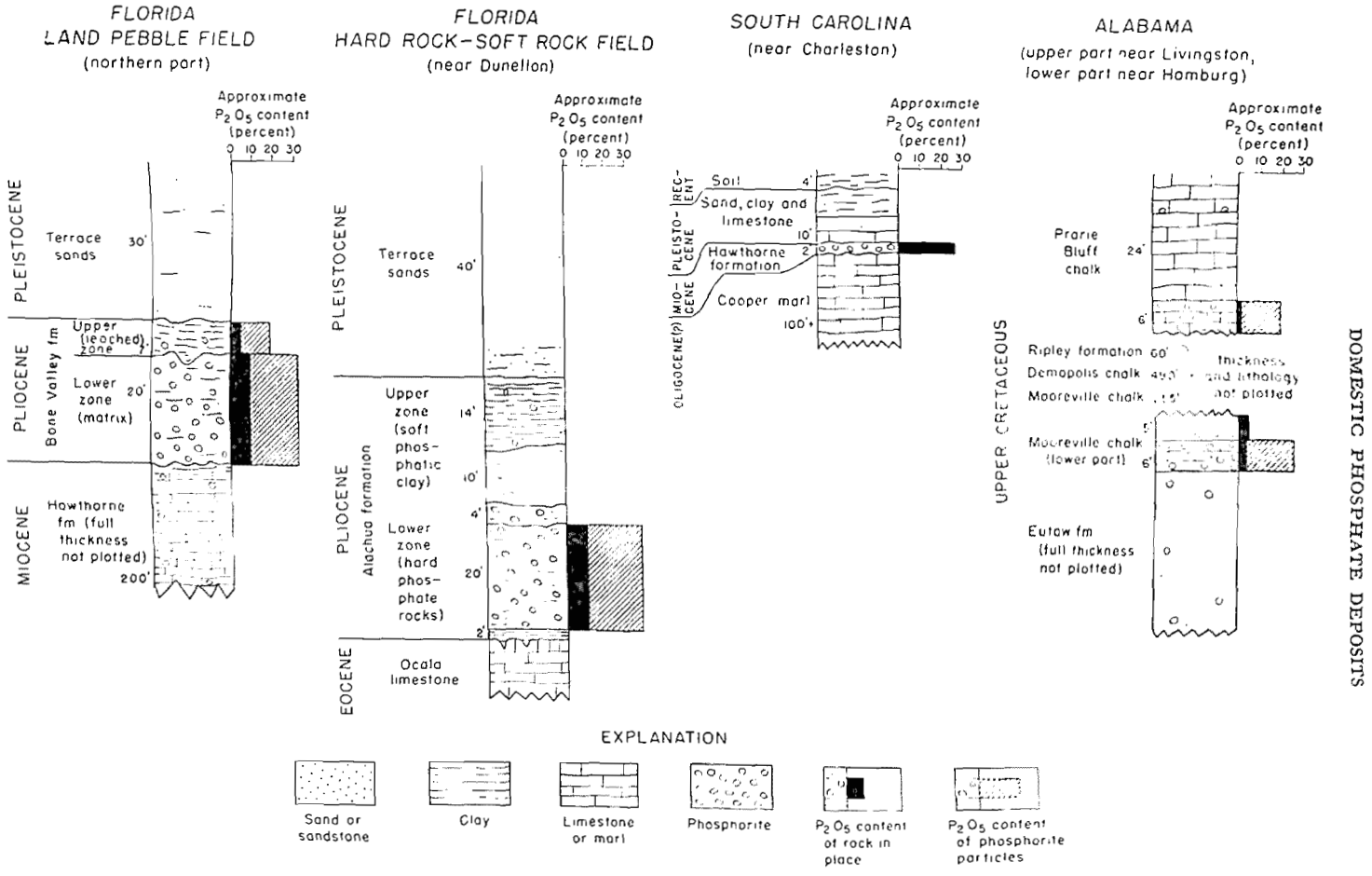


FIG. 2. Typical sections of phosphatic formation on the southeastern Costal Plain. (Data derived from the following sources: Florida land-pebble field, unpublished U. S. Geological Survey data; Florida hardrock field, from Vernon, 1947, supplemented by U. S. Geological Survey Data; South Carolina, from G. S. Rogers, 1915; Alabama, from Smith, 1892, supplemented by information furnished by Watson Monroe.)

relative abundance of phosphorite particles in the matrix, the content of recoverable phosphorite ranges from about 500 tons to 35,000 tons per acre and averages about 5000 tons per acre in the minable part of the field.

The P_2O_5 content of the phosphate particles ranges from about 28 to 36 per cent. The P_2O_5 content is higher, 32 to 36 per cent, in the north-

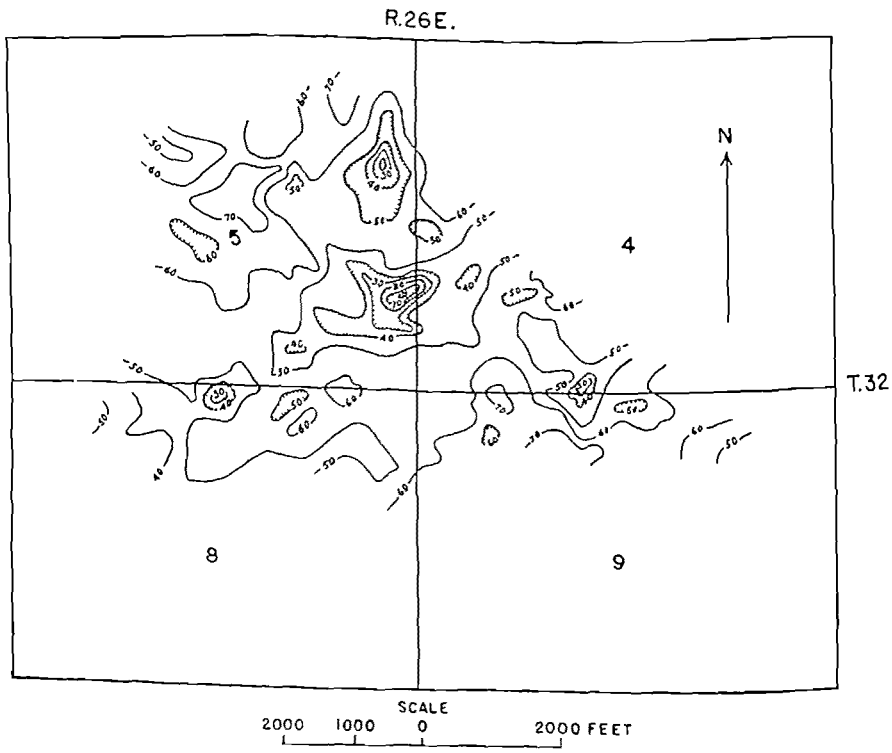


FIG. 3. The surface of the Hawthorn formation, Old Colony mine, American Cyanamid Co., land-pebble phosphate field, Florida. Contour interval 10 feet. (Data furnished by the American Cyanamid Co.)

ern part of the field, and generally lower, 28 to 32 per cent, in the southern part. The northern part may be further subdivided into two general areas: a central area where the phosphate particle size is generally coarse and the P_2O_5 content of the particles is 32 to 33 per cent; and a peripheral area where the particle size is finer and the P_2O_5 content of the particles is 33 to 36 per cent (Fig. 4). D. F. Davidson and F. N. Houser (unpublished U. S. Geological Survey reports) have shown that the coarser particles are found on highs on the Hawthorn formation.

Mining, at present restricted to the northern part of the field, is entirely by large-scale, low-cost open-pit methods. The phosphorite particles are separated from the matrix by washing, screening, and flotation.

The upper part of the Bone Valley has been irregularly leached and altered. This leached zone generally ranges from 1 to 15 feet in

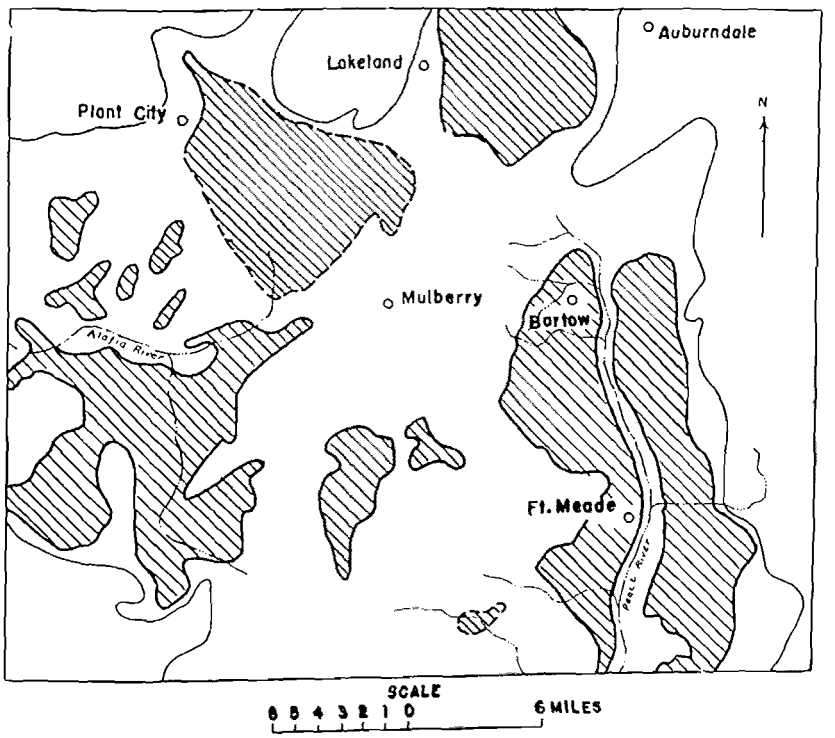


FIG. 4. Distribution of coarse (+1.2 mm.) and fine (−1.2 to +0.1 mm.) phosphatic particles in the land-pebble phosphate field, Florida. (The areas where the ratio of coarse to fine particles is less than one are ruled. The light solid line indicates the limits of minable phosphate deposits.)

thickness; however, it may be as thick as 50 feet. The leached zone is generally thickest on topographic highs. From 70 to 80 per cent of the leached-zone material is medium to coarse quartz sand and the remainder is minus 150-mesh particles. The fines consist mainly of the aluminum phosphate wavellite and the calcium aluminum phosphate psuedowavellite; minor amounts of carbonate-fluorapatite and kaolin are also present. The leached-zone material is stripped and discarded. The minus 150-mesh fraction is easily separated from the quartz sand,

and contains 15 to 30 per cent P_2O_5 and a similar amount of Al_2O_3. It is possible that the minus 150-mesh fraction may be utilized eventually as a source of phosphate or alumina.

2. *Florida Hard-Rock Field*

The hard-rock deposits in northwestern peninsular Florida have produced about 13.5 million long tons of phosphate rock from 1889, when mining began, to 1949. Production in recent years, however, has dropped to a rate of 25,000 to 50,000 tons a year.

The hard-rock deposits are in the Alachua formation, of Pliocene age, which outcrops within a belt 5 to 30 miles wide extending about 150 miles southeastward from Tallahassee to the northern part of Pasco County (Mansfield, 1940, 1942a). The Alachua formation rests on the croded surfaces of parts of the Ocala and Suwanee limestones of Eocene and Oligocene age, respectively (Sellards, 1915). It is probably the nonmarine equivalent, in both age and source, of the Bone Valley formation and consists mostly of the collapsed and compacted residue of the Hawthorn formation of Miocene age (Mansfield, 1940; Cooke, 1945). The phosphate present originally as nodules in the Hawthorn formation has been largely dissolved and redistributed as replacements of limestone blocks and clay. Some of the immediately underlying limestones of the Ocala and Suwanee have also been phosphatized.

Most of the hard-rock deposits occur in the lower part of the Alachua (Fig. 2), and are associated with fragments of chert and silicified limestone in a matrix of fuller's earth, quartz sand, and phosphatic clay (Vernon, 1951). The phosphate is in the form of phosphatic clay, detrital pebbles of phosphorite, phosphatized fragments or blocks of limestone, and irregular masses or plates. Individual deposits are characteristically small and irregular in shape, but they contain 33 to 36 per cent P_2O_5 or more.

The hard-rock deposits are mined by cheap open-pit methods, and the rock is concentrated by washing and screening. Because of the small size and irregular distribution of the remaining deposits, prospecting costs are much higher than in the land-pebble field. The coarse size and high phosphate content of the hard-rock make it an ideal furnace feed and a small continuing production may be expected for that purpose from the Dunellon area.

The upper part of the Alachua formation consists of phosphatic clay and fine-grained quartz sand. This zone has been little studied, but it is possible that it is a leached-zone analogous to that in the land-pebble field. This zone, together with slime derived from the washing of the hard-rock deposits, yields what is known in the industry as soft-

rock phosphate. About a million tons of soft-rock has been produced from this field.

3. *Tennessee Brown-Rock Field*

The Tennessee brown-rock field produced 33.3 million long tons of phosphate rock from 1896, when mining began, through 1949. Its production in 1949 was about 1.4 million tons. It thus ranks second to the Florida land-pebble field in total as well as current annual production.

The brown-rock deposits are composed of residual phosphorite particles, quartz sand, and clay derived from the chemical decomposition of

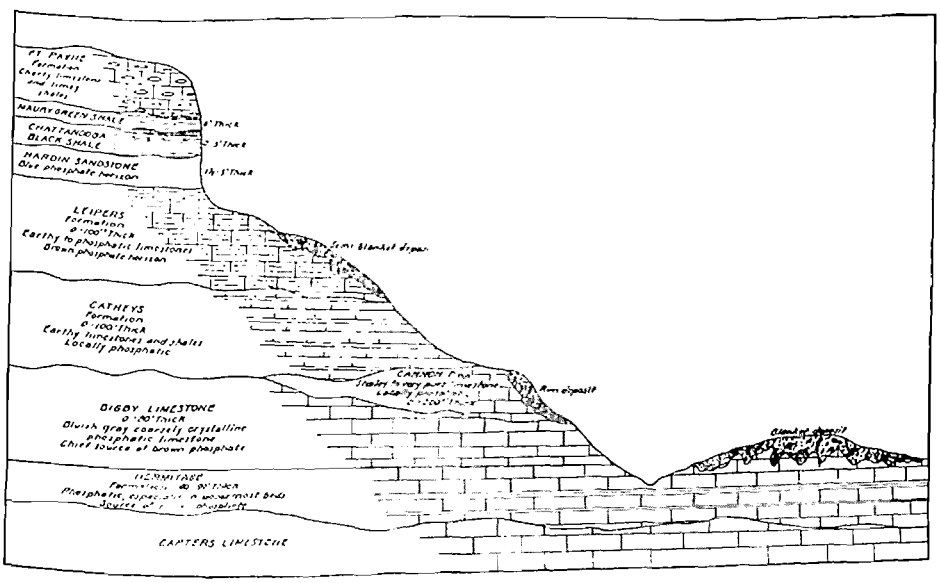


FIG. 5. Mode of occurrence of Tennessee blue- and brown-rock phosphate deposits (from Smith and Whitlatch, 1940, p. 44).

platform-type phosphatic limestones of Ordovician age (Hayes and Ulrich, 1903; Smith and Whitlatch, 1940; Burwell, 1950). These phosphatic limestones, deposited in shallow, platform seas, have been gently uplifted, arched, and exposed by erosion in the central (Nashville) basin. The phosphatic formations are of wide extent—the Kentucky brown-rock deposits are derived from the same formations—but residual concentrations of present commercial value are found mainly in the vicinity of Columbia and Mount Pleasant, Maury County, Tenn.

The local distribution of the deposits conforms in a general way to the outcrops of the limestones from which they were derived. The thickest are found as fillings in corroded joints or "cutters" lying be-

tween limestone horses. The most extensive (blanket) deposits occur on flat ground underlain by the Hermitage, Bigby, and Leipers limestones. Less extensive deposits are found as rims on hillside outcrops (Fig. 5).

Although most of the phosphate particles are physical residues from the limestones, in areas of deeper weathering the phosphatic particles in the upper parts of the deposits have been dissolved and redeposited as cement or as plate-like replacements of other materials in the lower parts. Such plate-rock is rich in P_2O_5 and has been selectively mined in many places. The uncemented rock as mined contains about 15 to 30 per cent P_2O_5. Most of it is concentrated by washing, screening, and, in some places, by flotation, to a product containing 30 to 36 per cent P_2O_5, but some of the rock is used without beneficiation as electric furnace feed. All of the brown-rock is mined by open-cut methods.

1. The Western Field

The western phosphate field is one of the largest in the world, both in size and in reserves (Mansfield, 1927; McKelvey, 1949). Mining operations date back to 1906 but only about 6 million long tons were produced through 1949. The growing importance of the field, however, is indicated by the fact that 55 per cent of the total production came during the 1946–1949 period.

The western deposits are marine. Some are found in the Brazer limestone of Carboniferous age but the most extensive, and the only ones we shall consider here, occur in the Phosphoria formation of Permian age and its partial stratigraphic equivalent in Utah, the Park City formation. These formations crop out over an area of about 135,000 square miles in Montana, Idaho, Wyoming, Utah, and Nevada (Fig. 6). The deposits in the eastern part of the field are of the platform type, and those in the western part are of the geosynclinal type (McKelvey *et al.*, 1953).

The rocks of Permian age and the overlying and underlying sediments have been compressed, folded, uplifted, and exposed by erosion since their widespread deposition on the sea floor. Although deformation affected the whole area, it was more intense in the western part. The field may thus be divided into an eastern part of simple structure and a western part of complex structure (Fig. 6). In the eastern part, the folds are of the dome and basin type. The beds generally dip less than 30 degrees, and closely spaced faults of large displacement are uncommon. The folds are randomly oriented and the outcrop belts of the phosphatic rocks are widely separated. In the western area, on the other hand, the folds are tightly compressed and the beds generally dip at high angles, commonly more than 45°. The folds have a parallel orien-

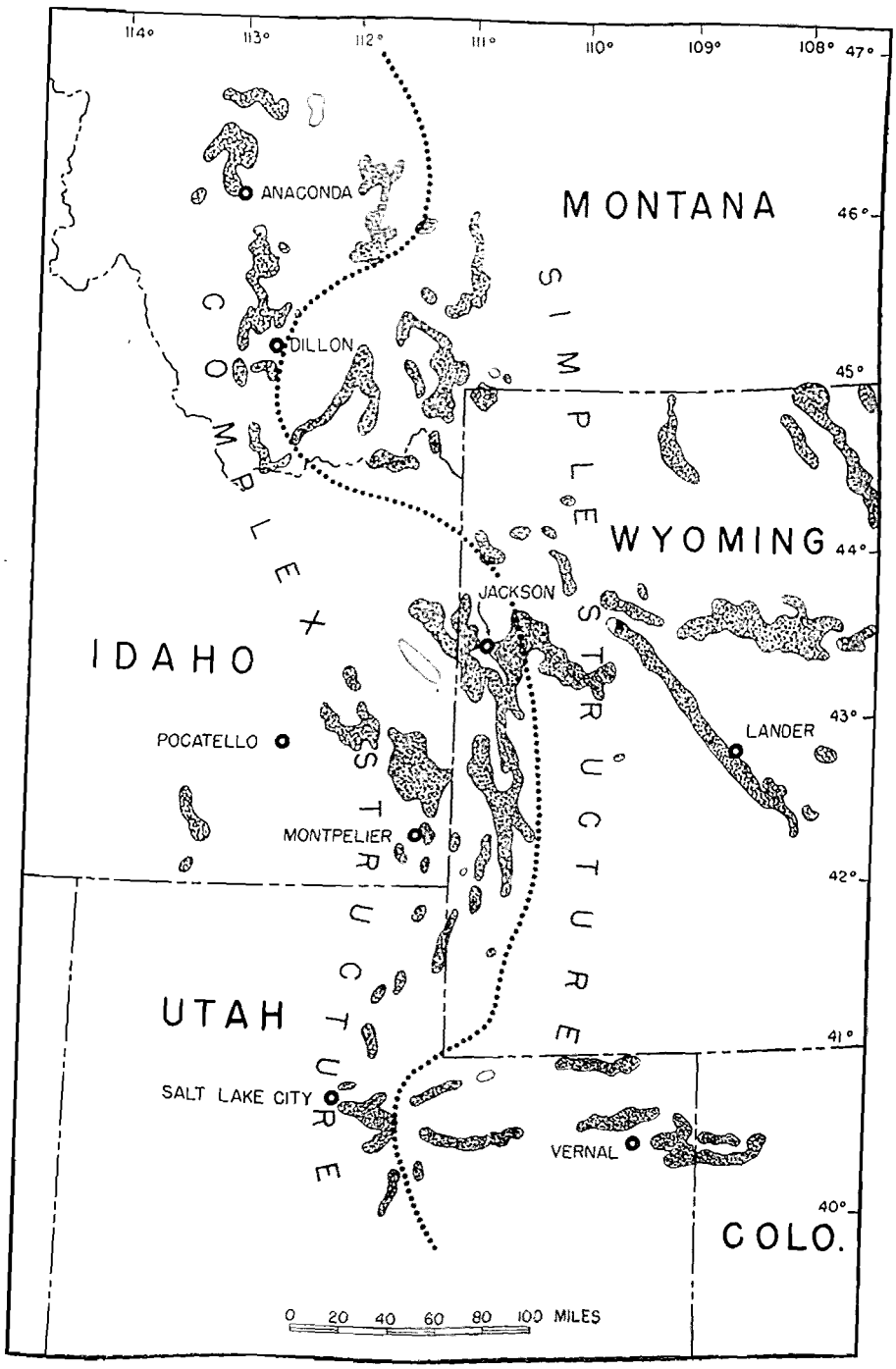


FIG. 6. Distribution of outcrops of Permian phosphatic rocks in the western field. (Dotted line marks the approximate boundary between areas of simple and complex structure.)

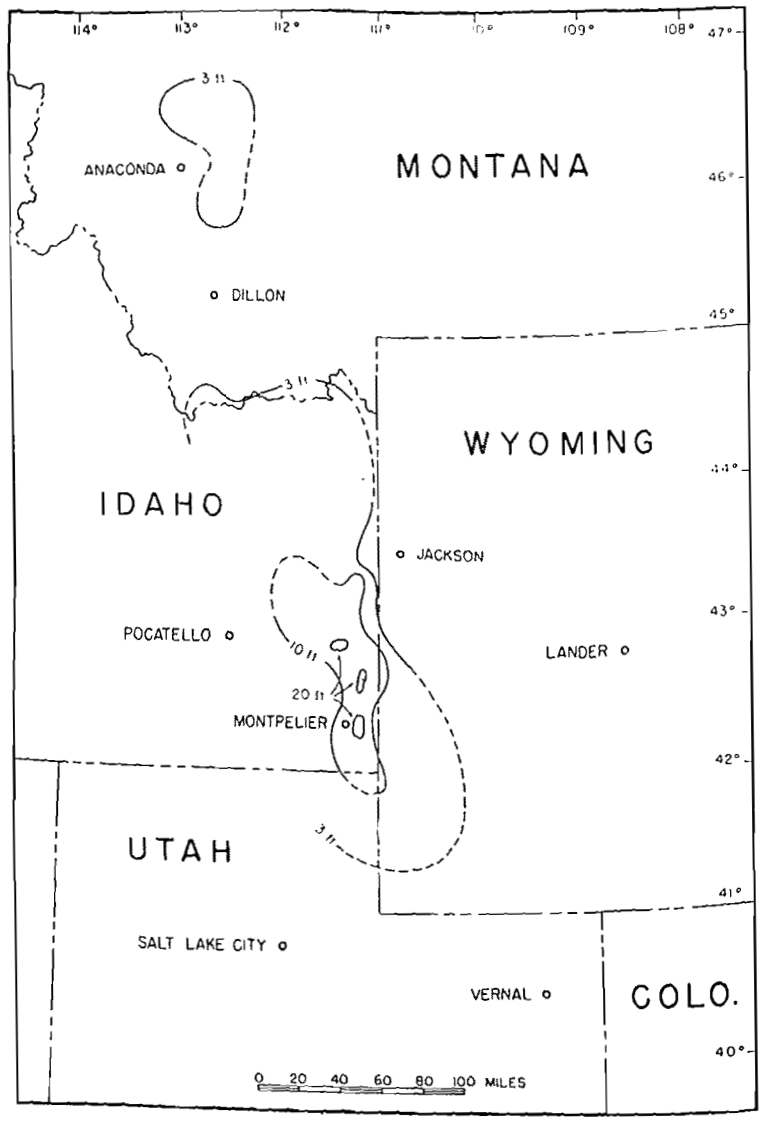
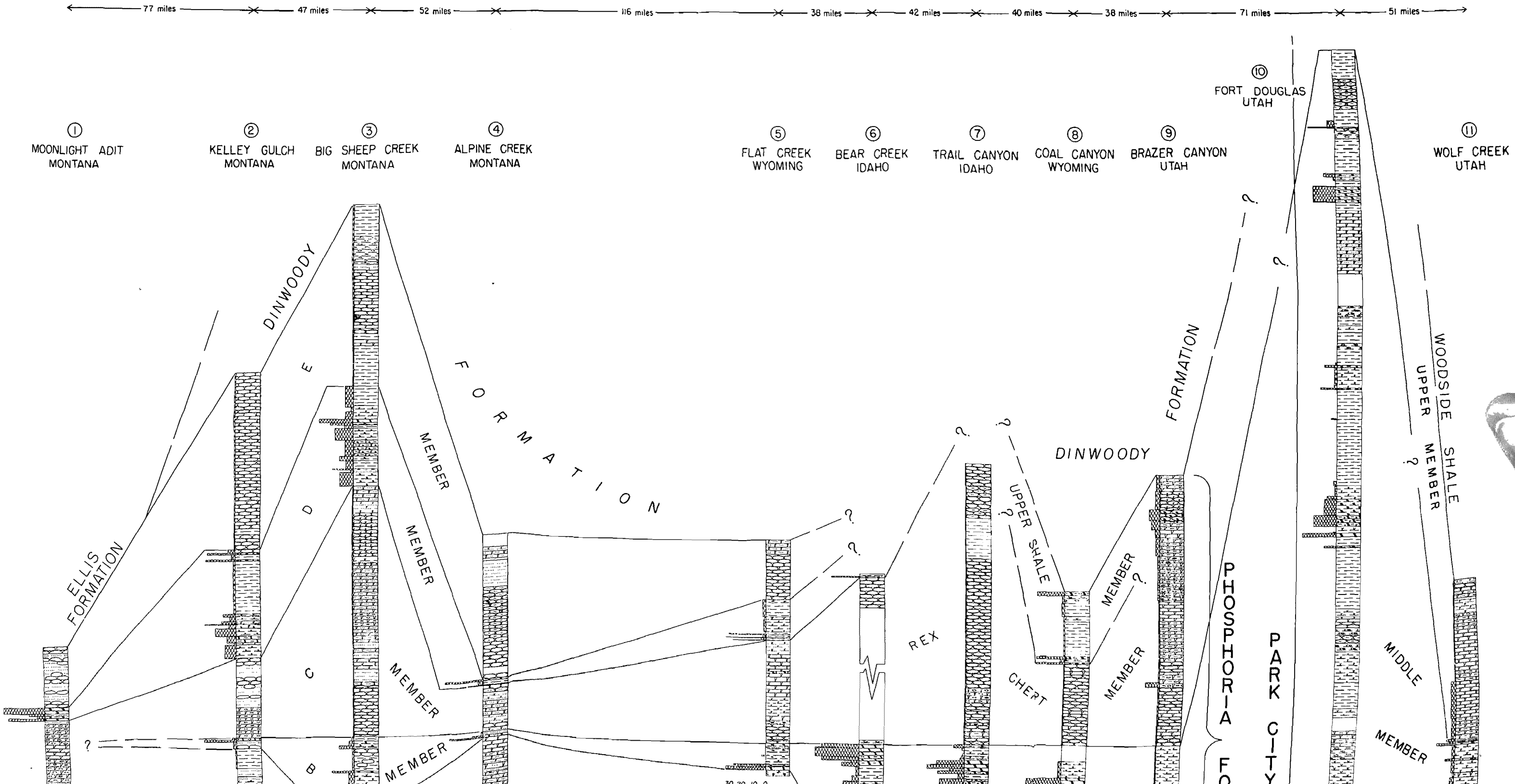


FIG. 8. Thickness in feet of beds in the Phosphoria and Park City formations containing more than 31 per cent P_2O_5.

tation. Many are mashed and are broken by faults of both large and small displacement. Because of the close, intense folding and repetition by faulting, outcrop belts of the phosphatic rocks are close together.

Many layers of these formations of Permian age are phosphatic, but the most important ones are found in the lower, phosphatic shale member of the Phosphoria formation (Fig. 7). These layers range widely in thickness and P_2O_5 content over the field, but the variation


77 miles
47 miles
52 miles
116 miles
38 miles
42 miles
40 miles
38 miles
71 miles
51 miles
① MOONLIGHT ADIT MONTANA
② KELLEY GULCH MONTANA
③ BIG SHEEP CREEK MONTANA
④ ALPINE CREEK MONTANA
⑤ FLAT CREEK WYOMING
⑥ BEAR CREEK IDAHO
⑦ TRAIL CANYON IDAHO
⑧ COAL CANYON WYOMING
⑨ BRAZER CANYON UTAH
⑩ FORT DOUGLAS UTAH
⑪ WOLF CREEK UTAH
ELLIS FORMATION
DINWOODY FORMATION
E
D
C
B
MEMBER
MEMBER
MEMBER
MEMBER
REX CHERT
UPPER SHALE MEMBER
DINWOODY FORMATION
MEMBER
PHOSPHORIA FORMATION
PARK CITY FORMATION
WOODSIDE SHALE
UPPER MEMBER
MIDDLE MEMBER
?

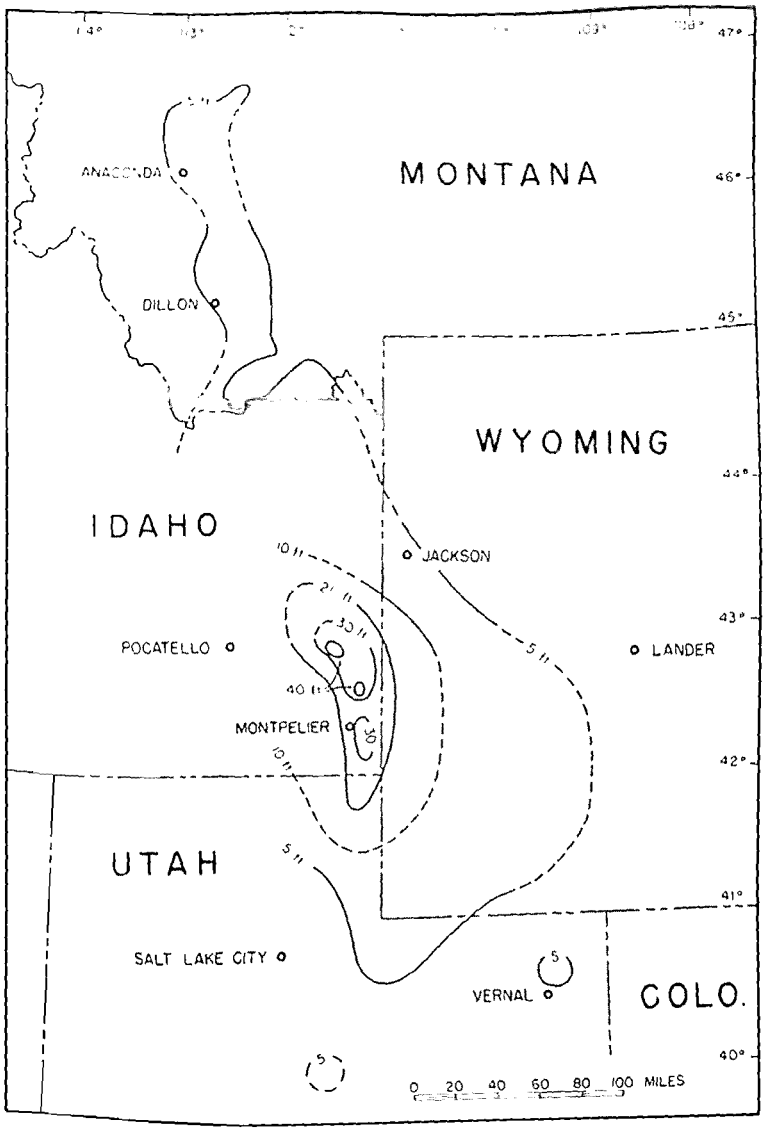


FIG. 9. Thickness in feet of beds in the Phosphoria and Park City formations containing more than 25 per cent P_2O_5.

for the most part is systematic. As shown in Figs. 8 and 9, the thickness and quality of the phosphatic rocks increase westward to a maximum in southeastern Idaho. Information is sparse for areas further west in Idaho, but the thickness and quality appear to decrease.

Rocks of two qualities are mined in the western field. The principal production in the past has been of acid-grade rock, which contains 31 per cent or more P_2O_5 in layers about 3 feet in thickness. Rocks of this

quality and thickness are found in northern Utah, westernmost Wyoming, southeastern Idaho, and southwestern Montana (Fig. 8); although acid-grade rock is mined at only five localities, many others contain minable deposits. The second type of rock, furnace-grade, has been produced in important quantities only since 1949, when the first of the eight electric furnaces now in operation (or construction) in the field was built at Pocatello, Idaho, by the West Vaco Co. Furnace-grade rock contains about 24 per cent or more P_2O_5 and occurs in beds 8 feet or more thick. Such deposits are found in essentially the same areas where acid-grade rocks are found, but present production is restricted to two localities in southeastern Idaho and one in western Montana. For the most part, rocks of both qualities must meet the specified P_2O_5 content as mined. Their high degree of cementation and hardness does not recommend them for low-cost beneficiation.

Most rich and thick deposits can be mined only by underground methods because of the structural complexities already described. There are a few high-grade deposits amenable to strip-mining in southeastern Idaho and western Wyoming, but most of these are found in the eastern part of the field (Fig. 6), where the thickness and quality are too low to make this mining profitable now. Some of these deposits, such as those near Vernal, Utah, may, however, be important producers in the future.

5. *Other Deposits*

None of the other phosphate deposits in this country is apt to be an important producer in the foreseeable future, but a few remarks on distribution may serve as background for appreciation of our phosphate resource potential. A more complete summary of information on these deposits may be found in papers by Jacob *et al.* (1933), Mansfield (1940), and Jacob (1953) p. 117.

a. Atlantic and Gulf Coastal Plain. Phosphate deposits are found in rocks of Cretaceous or Tertiary age on the Atlantic and Gulf Coastal Plain in nearly every state from Massachusetts to Texas. The most widespread are those of the marine platform type associated with glauconite sand, quartz sand, and limestone. The most important deposit to be mined in the far distant future is the Hawthorn formation of Miocene age, which contains phosphorite particles over nearly its whole extent in Florida, Georgia, and South Carolina. The most productive deposits on the Coastal Plain, aside from current producers already described, are the river-pebble and land-rock phosphate deposits in South Carolina (Rogers, G. S., 1915) and the river-pebble de-

posits in Florida (Mansfield, 1942a). The South Carolina land-rock deposits, which consist of phosphatized rock in the Hawthorn formation, produced 9.3 million tons between 1867 and 1925. The South Carolina and Florida river-pebble deposits, both derived directly or indirectly through erosion of the Hawthorn formation, produced 4.1 and 1.3 million tons prior to 1910 and 1914, respectively.

Other deposits on the Coastal Plain are found in Massachusetts (Shaler, 1888); New Jersey (Mansfield, 1922); North Carolina (Brown, 1905); Georgia (McCallie, 1896); Alabama (Smith, 1892; Monroe, 1941); Mississippi (Stephenson and Monroe, 1940; Day, 1886); Arkansas (Branner and Newsom, 1902); and Texas (Stephenson, 1929; Gardner, 1933). Only the deposits in South Carolina, Georgia, and Alabama have been mined and their production has been negligible.

b. Continental Interior and Eastern Mountain Regions. Igneous apatite deposits associated with ilmenite in Virginia (Stose, 1914; Watson and Taber, 1913) yielded small production until 1947 when mining ceased (Johnson and Tucker, 1950). Wilbur (1883) reports that small amounts of apatite associated with magnetite were recovered in New York and New Jersey. Similar deposits are found in Massachusetts (Wilbur, 1883) and Missouri (Blake, 1893).

The most widespread deposits in the continental interior are the marine platform-type, associated with limestones of Paleozoic age, glauconite sands, or black shales. Examples include deposits in the Oriskany formation of Devonian age in New York (Hopkins, 1914), Pennsylvania (Ihlseng, 1896), and Virginia (Stose, 1914); the Hardin sandstone member of the Mississippian Chattanooga shale in Tennessee (Smith and Whitlatch, 1940) and Georgia (Hayes, 1895); the Maquoketa shale of Ordovician age in Illinois (Weller, 1907), Iowa (Bain, 1906), and Wisconsin (Grant and Burchard, 1907); several formations of Ordovician horizons in eastern Minnesota (Pettijohn, 1926) and Arkansas (Branner and Newsom, 1902; Waggaman, 1912); black shales in the Pennsylvanian of Kansas (Runnels, 1949) and Oklahoma (Oakes, 1938); and limestones in the Permian in El Paso and Hudspeth Counties, Texas (A. L. Slaughter, personal communication). Only the deposits in Tennessee and Arkansas have been mined. The Tennessee deposits, known as the blue-rock phosphates, produced 1.3 million tons; the Arkansas deposits produced about 32,000 tons.

Secondary deposits, concentrated during the weathering of the platform-type rocks, occur in north-central Kentucky (Phalen, 1915); Tennessee (Smith and Whitlatch, 1940); northern (Ross, B. B., 1900) and

north-central (Phalen, 1912) Alabama; and Pennsylvania (Stose, 1907). The Kentucky and northern Alabama deposits are similar to the brown-rock phosphates of Tennessee and are derived from the same limestones, which are Ordovician in age. The Tennessee white-rock deposits are phosphatized limestones formed from the leaching of the overlying blue-rock deposits. The north-central Alabama and the Pennsylvania deposits are composed mainly of the aluminum phosphate wavellite formed through weathering of the phosphatic rocks of Ordovician and Devonian age in those areas. The Kentucky brown-rock, the Tennessee white-rock, and Pennsylvania wavellite deposits have produced a few thousand tons each.

Numerous deposits of bat guano in caves in central Texas and New Mexico have been reported (Phillips, 1901; Schoch, 1918). Small quantities of the material have been mined from some of them.

c. Western States. In addition to the previously described extensive phosphate deposits in the Phosphoria formation, marine phosphates are found in the Swan Peak quartzite of the Ordovician (Mansfield, 1927) and the Brazer limestone of the Mississippian in northern Utah (Blackwelder, 1910) and southeastern Idaho (Mansfield, 1927); the Deseret limestone of the Mississippian in Utah (Gilluly, 1932); scattered localities in eastern Nevada (possibly equivalents of the Phosphoria formation); and at numerous localities in the rocks of Tertiary age in California (Rogers, A. F., 1944; Emery and Dietz, 1950; Reed, 1933; Hoots, 1931; Woodring *et al.*, 1946). None of these deposits has ever been mined.

Igneous apatite deposits are found in Colorado (Jacob *et al.*, 1933); Utah (Blake, 1893); and Nevada (Stone, 1920). None of these deposits has been mined either.

IV. Reserves

Reserves of domestic deposits are listed in Table III. Most of these estimates were published earlier by Mansfield (1942b) and Jacob (1953). The estimates for the Florida land-pebble field and the western field, however, are revised, preliminary estimates, based on recent, unpublished results of the U. S. Geological Survey investigations. Because the synthesis of our Florida data is well advanced, the estimates presented here are nearly final. As the compilation of new data on western deposits is not complete, the estimates presented are by no means final; but they do indicate order of magnitude.

An effort has been made in this compilation to separate minable reserves from resources too low in quality or too deep to be mined

economically at the present time. Some of the reserves included in the second category are not much less valuable than those in the first. For example, the tonnages in the western field listed as not minable now are of the same thickness and quality as those considered minable but lie at greater depths below the surface. A much larger volume of material of lower quality is not reported. Others, such as the Hawthorn deposits and Tennessee limestone, are of much lower quality than those which are mined in this country. It is safe to assume, however, that many of these deposits as well as tremendous reserves in other leaner deposits not reported will be mined later when the currently minable deposits are exhausted. The separation between minable and unminable deposits shown here is thus not of long-term significance, but emphasizes the fact that some of our deposits cost more to mine than others.

The estimates presented show that our reserves of minable phosphates (measured, indicated, and inferred categories) total about 5 billion tons of rock containing about 1.5 billion tons of P_2O_5. Known deposits available for mining when these are exhausted total nearly 50 billion tons of rock containing 12 billion tons of P_2O_5. At the present rate of consumption these resources will supply our needs for about 4500 years. It is common knowledge that present consumption of phosphate is not adequate to replace the phosphate annually removed from the soil by crops and erosion. These estimated reserves indicate that our resources will support a much increased production.

This picture of large reserves is made even brighter by the probability that, despite the long history of prospecting in this country, new discoveries of phosphate deposits will be made. Particularly promising are possibilities for discovering high-grade igneous apatite deposits in areas such as Magnet Cove, Arkansas; southwest-central Montana; central Colorado; southern California; and other alkalic igneous rock provinces. It seems likely, too, that geosynclinal phosphorites may be found, particularly at depth on the Gulf Coastal Plain.

V. Acknowledgments

Many of our colleagues on the U. S. Geological Survey are participating in current phosphate investigations in the western and Florida fields. It is a pleasure to acknowledge their contributions to the fund of new information drawn on in this summary, even though it is not possible to mention them all by name. The recent investigations of domestic deposits have been supported partly by the Atomic Energy Commission and the Bureau of Reclamation. The support of these agencies is gratefully acknowledged.

References

ADAMS, F. D., and BARLOW, A. E. 1910. Geology of the Haliburton and Bancroft areas, Province of Ontario. *Canada Geol. Survey, Mem.* 6: 383.

ALTSCHULER, Z. S., and CISNEY, E. A. 1952. X-ray evidence of the nature of carbonate-apatite. *19th Intern. Geol. Cong. Proc.*, p. 75.

BAIN, H. F. 1906. Zinc and lead deposits of the upper Mississippi Valley. *U. S. Geol. Survey Bull.* **294**: 25.

BLACKWELDER, ELIOT. 1910. New light on the geology of the Wasatch Mountains. Utah. *Bull. Geol. Soc. Amer.* **21**: 526–527.

BLAKE, W. P. 1893. Association of apatite with beds of magnetite. *Am. Inst. Mining Engrs. Trans.* **21**: 159–160.

BRANNER, J. C., and NEWSOM, J. F. 1902. The phosphate rocks of Arkansas. *Arkansas Agr. Expt. Sta. Bull.* **74**: 61–123.

BROWN, L. P. 1905. The phosphate deposits of the southern states. *Eng. Assoc. South Trans.* **15**: 53–128.

BURWELL, H. R. 1950. Brown phosphate rock in Tennessee. Symposium on mineral resources of the southeastern states, 1949 proceedings, pp. 128–131, The University of Tennessee Press, Knoxville, Tennessee.

CADY, J. G., HILL, W. L., MILLER, E. V., and MAGNESS, R. M. 1952. Occurrence of beta tricalcium phosphate in northern Mexico. *Am. Mineralogist* **37**: 180–183.

CATHCART, J. B. 1950. Notes on the land-pebble phosphate deposits of Florida. Symposium on mineral resources of the southeastern states, 1949 proceedings, pp. 132–151, The University of Tennessee Press, Knoxville.

CATHCART, J. B., BLADE, L. V., DAVIDSON, D. F., and KETNER, K. B. 1953. The geology of the Florida land-pebble phosphate deposits. *19th Intern. Geol. Congr. Proc.* In press.

CAYEUX, LUCIEN. 1931. Introduction à l'étude petrographique des roches sédimentaires. Paris, Ministère des Travaux Publics.

CAYEUX, LUCIEN. 1941. Les phosphates de chaux sédimentaires de France et d'Outre-Mer. *L'Afrique Septentrionale* **2**: 351–659.

COOKE, C. W. 1945. Geology of Florida. *Florida Geol. Survey Bull.* **29**: 339 pp.

DAVIES, K. A. 1947. The phosphate deposits of the Eastern Province, Uganda. *Econ. Geol.* **42**: 137–146.

DAY, D. T. 1886. Phosphate rock. *U. S. Geol. Survey Mining Resources of the U. S., calendar year* **1885**: 445–458.

ELDRIDGE, G. H. 1893. A preliminary sketch of the phosphates of Florida. *Am. Inst. Mining Engrs. Trans.* **21**: 196–231.

EMERY, K. O., and DIETZ, R. S. 1950. Submarine phosphorite deposits off California and Mexico. *Calif. J. Mines Geol.* **46**: 7–15.

FIVEG, M. P. 1937. The apatite deposits of the Khibinian tundras. *Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)* **142**: 8–21, published for 17th International Geological Congress, Leningrad.

FRONDEL, CLIFFORD. 1943. Mineralogy of the calcium phosphates in insular phosphate rock. *Am. Mineralogist* **28**: 215–232.

GARDNER, JULIA. 1933. The Midway group of Texas. *Texas University Bull.* **3301**: 403 pp.

GILLULY, JAMES. 1932. Geology and ore deposits of the Stockton and Fairfield quadrangles, Utah. *U. S. Geol. Survey Profess. Paper* **173**: 25.

GOLDMAN, M. I. 1922. Basal glauconite and phosphate beds. *Science*, [n.s.] **56**: 171–173.

GORDON, S. G. 1925. Variscite and other phosphates from Moore's Mill, Cumberland County, Pa. *Proc. Acad. Nat. Sci. Phila.* **77**: 4–8.

GRAMMONT, M. H. 1924. Étude sur les phosphates naturels—Recherche et dosage des métaux contenus en petite quantité dans ces minéraux. *Bull. soc. chim. France* **35**: 405–408.

GRANT, U. S., and BURCHARD, E. F. 1907. Description of the Lancaster and Mineral Point quadrangles. *U. S. Geol. Survey Folio* **145**: 14 pp.

HARADA, Z. 1938. Beiträge zur Kenntnis der optischen und chemischen Eigenschaften des Apatits von Kurokuro, Kanagawa Präfektur. *J. Faculty Sci. Hokkaido Imp. Univ.* **4**: 11–16.

HAYES, C. W. 1895. The Tennessee phosphates. *U. S. Geol. Survey Ann. Rept.* **16** (pt. 4): 610–630.

HAYES, C. W., and ULRICH, E. O. 1903. Description of the Columbia quadrangle. *U. S. Geol. Survey Folio* **95**: 6 pp.

HÉBERT, CLAUDE. 1947. Contribution à l'étude de la chimie des phosphates de calcium. *Ann. mines*, **136**: No. 4, 5–93.

HENDRICKS, S. B., JEFFERSON, M. E., and MOSELY, V. M. 1932. The crystal structure of some natural and synthetic apatite-like substances. *Z. Krist.* **81**: 351–369.

HERTZOG, E. S. 1935. A study of the occurrence and amenability to leaching of the phosphorus compounds in some red iron ores of Alabama. *U. S. Bur. Mines Repts. Invest.* **3294**: 9 pp.

HILL, W. L., MARSHALL, H. L., and JACOB, K. D. 1932. Minor metallic constituents of phosphate rock. *Ind. Eng. Chem.* **24**: 1306–1312.

HOOTS, H. W. 1931. Geology of the eastern part of the Santa Monica Mountains, Los Angeles County, California. *U. S. Geol. Survey Profess. Paper* **165C**: 105–106.

HOPKINS, T. C. 1914. The geology of the Syracuse quadrangle. *N. Y. State Museum Bull.* **171**: 80 pp.

HUTCHINSON, G. E. 1950. Survey of contemporary knowledge of biogeochemistry. 3. The biogeochemistry of vertebrate excretion. *Bull. Am. Museum Nat. Hist.* **96**: 554 pp.

IHLSENG, M. C. 1896. A phosphate deposit in Juniata County. *Pennsylvania State Coll. Agr. Expt. Sta. Bull.* **34**: 955–957.

JACOB, K. D. 1953. Phosphate resources and manufacturing facilities in the United States. *In* Fertilizer Technology and Resources, pp. 117–159. K. D. Jacob, Editor. Academic Press, New York.

JACOB, K. D., HILL, W. L., MARSHALL, H. L., and REYNOLDS, D. S. 1933. The composition and distribution of phosphate rock with special reference to the United States. *U. S. Dept. Agr. Tech. Bull.* **364**: 90 pp.

JOHNSON, B. L., and TUCKER, E. M. 1950. Phosphate rock. *U. S. Bur. Mines, Minerals Yearbook* **1948**: 1023–1040.

JOHNSON, B. L., and TUCKER, E. M. 1951. Phosphate rock. *U. S. Bur. Mines, Minerals Yearbook* **1949**: 993–1012.

KAZAKOV, A. V. 1937. The phosphorite facies and the genesis of phosphorites. *Trans. Sci. Inst. Fertilizers Insectofungicides (U.S.S.R.)* **142**: 8–21, published for 17th International Geological Congress, Leningrad.

LINDGREN, WALDEMAR. 1933. Mineral Deposits. 4th ed., 930 pp., McGraw-Hill Book Co., New York.

MANSFIELD, G. R. 1922. Potash in the greensands of New Jersey. *U. S. Geol. Survey Bull.* **727**: 146 pp.

MANSFIELD, G. R. 1927. Geography, geology and mineral resources of part of southeastern Idaho. *U. S. Geol. Survey Profess. Paper* **152**: 409 pp.

MANSFIELD, G. R. 1940. Phosphate deposits of the United States. *Econ. Geol.* **35**: 405–429.

MANSFIELD, G. R. 1942a. Phosphate resources of Florida. *U. S. Geol. Survey Bull.* **934**: 82 pp.

MANSFIELD, G. R. 1942b. Recent studies of reserves of domestic phosphate. *Trans. Am. Inst. Mining Met. Engrs.* **148**: (reprint of *Tech. Publ.* 1208) 10 pp.

MATSON, G. C. 1915. The phosphate deposits of Florida. *U. S. Geol. Survey Bull.* **604**: 101 pp.

MCCALLIE, S. W. 1896. A preliminary report on a part of the phosphates and marls of Georgia. *Georgia Geol. Survey Bull.* **5A**: 101 pp.

MCCONNELL, D. 1943. Phosphatization at Malpelo Island, Columbia. *Bull. Geol. Soc. Am.* **54**: 707–716.

MCKELVEY, V. E. 1949. Geological studies of the western phosphate field. *Trans. Am. Inst. Mining Met. Engrs.* **184**: 270–279.

MCKELVEY, V. E., and NELSON, J. M. 1950. Characteristics of marine uranium-bearing sedimentary rocks: *Econ. Geol.* **45**: 35–53.

MCKELVEY, V. E., SWANSON, R. W., and SHELDON, R. P. The Permian phosphorite deposits of western United States. *19th Intern. Geol. Congr. Proc.* (In press).

MONROE, W. H. 1941. Notes on deposits of Selma and Ripley age in Alabama. *Alabama Geol. Survey Bull.* **48**: 150 pp.

OAKES, M. C. 1938. Phosphate. *Oklahoma Geol. Survey Mining Rept.* **2**: 13 lvs.

OERTEL, A. C., and STACE, H. T. C. 1947. A spectrochemical survey of some phosphate rock and superphosphates. *J. Council Sci. Ind. Research* (Australia) **20**: 110–113.

PETTIJOHN, F. J. 1926. Intraformational phosphate pebbles of the Twin City Ordovician, *J. Geol.* **34**: 361–373.

PHALEN, W. C. 1912. Bauxite and aluminum. *U. S. Geol. Survey Mineral Resources of U. S.* **1911**, pt. 1: 923–939.

PHALEN, W. C. 1915. Report on the phosphate rocks of central Kentucky. 80 pp. Frankfort, Kentucky.

PHILLIPS, W. B. 1901. The bat-guano caves of Texas. *Mines and Minerals* **21**: 440–442.

REED, R. D. 1933. Geology of California. 355 pp. American Association of Petroleum Geologists, Tulsa, Oklahoma.

ROBINSON, W. O. 1948. The presence and determination of molybdenum and rare earths in phosphate rock. *Soil Sci.* **66**: 317–322.

RODGERS, JOHN. 1948. Phosphate deposits of former Japanese islands in the Pacific; a reconnaissance report. *Econ. Geol.* **43**: 400–407.

ROGERS, A. F. 1944. Pellet phosphate from Carmel Valley, Monterey County, California. *Calif. J. Mines Geol.* **40**: 411–421.

ROGERS, G. S. 1915. The phosphate deposits of South Carolina. *U. S. Geol. Survey Bull.* **580J**: 183–220.

RORTY, JAMES. 1946. Phosphorus; bottleneck of the world's hunger. *Harper's Magazine* **1158** (Nov.): 472–480.

ROSS, B. B. 1900. Composition and occurrence of phosphates in the Elk River Valley

near the state line, with a preliminary report on their extent and character by Henry McCalley. *Alabama Dept. Agr. Bull.* **14**: 15 pp.

Ross, C. S. 1941. Occurrence and origin of the titanium deposits of Nelson and Amherst Counties, Virginia. *U. S. Geol. Survey Profess. Paper* **198**: 59 pp.

Roundy, P. V. 1941. Phosphate investigation in Florida, 1934 and 1935. *U. S. Geol. Survey Bull.* **906F**: 267–345.

Runnels, R. T. 1949. Preliminary report on phosphate-bearing shales in eastern Kansas. *Kansas University, State Geol. Survey Bull.* **82**, pt. 2: 37–48.

Schoch, E. P. 1918. Chemical analyses of Texas rocks and minerals. *Texas Univ. Bull.* **1814**: 256 pp.

Sellards, E. H. 1915. The pebble phosphate of Florida. *Florida Geol. Survey, Ann. Rept.* **7**: 25–116.

Shaler, N. S. 1888. Report on the geology of Martha's Vineyard (Mass.). *U. S. Geol. Survey Ann. Rept. (1885–86)* **7**: 297–363.

Shand, S. J. 1932. The granite-syenite-limestone complex of Palabora, E. Transval. *Trans. Geol. Soc. S. Africa* **34**: 81–105.

Smith, E. A. 1892. On the phosphates and marls of Alabama. *Geol. Survey Alabama Bull.* **2**: 82 pp.

Smith, R. W., and Whitlatch, G. I. 1940. The phosphate resources of Tennessee. *Tennessee Dept. Conservation Div. Geol. Bull.* **48**: 444 pp.

Stephenson, L. W. 1929. Unconformities in the Upper Cretaceous series of Texas. *Bull. Am. Assoc. Petroleum Geol.* **13**: 1323–1334.

Stephenson, L. W., and Monroe, W. H. 1940. The Upper Cretaceous deposits. *Mississippi State Geol. Survey Bull.* **40**: 296 pp.

Stone, R. W. 1920. Phosphate rock. *U. S. Geol. Survey Mining Resources* **1917**, pt. 2: 7–18.

Stose, G. W. 1907. Phosphorus ore at Mount Holly Springs, Pa. *U. S. Geol. Survey Bull.* **315**: 474–483.

Stose, G. W. 1914. Phosphate deposits in southwestern Virginia. *U. S. Geol. Survey Bull.* **540L**: 383–396.

Sverdrup, H. U., Johnson, M. W., and Fleming, R. H. 1946. The Oceans, Their Physics, Chemistry, and General Biology. 1087 pp. Prentice-Hall, New York.

Tremearne, T. H., and Jacob, K. D. 1941. Arsenic in natural phosphorite and phosphate fertilizer. *U. S. Dept. Agr. Tech. Bull.* **781**: 39 pp.

Vernon, R. O. 1943. Florida mineral industry. *Florida Geol. Survey Bull.* **24**: 154–158.

Vernon, R. O. 1947. In *Southeastern Geo. Soc. 5th Field Trip Guidebook*, Dec. **1947**: 30.

Vernon, R. O. 1951. Geology of Citrus and Levy Counties, Florida. *Florida Geol. Survey Bull.* **33**: 181–208.

Vol'fkovich, S. 1945. Novyye resursy tukovoi promshlennosti (Fosfority Kara-Tau) *Planovoye Khozyaistvo*, Moscow, **5**: 48–60.

Volodchenkova, A. I., and Melentiev, B. N. 1943. Apatites of two textural types from apatite-nepheline rocks of Chibiny. *Compt. rend. acad. sciences U.R.S.S.* **39**: 34–35.

Waggaman, W. H. 1912. A report on the natural phosphates of Tennessee, Kentucky and Arkansas. *U. S. Dept. Agr. Bur. Soils Bull.* **81**: 36 pp.

Walker, T. L., and Parsons, A. L. 1926. Apatite, lepidomelane and associated minerals from Faraday township, Hastings County, Ontario. *Univ. of Toronto Geol. Studies* **22** (Contrib. to *Can. Mineralogy*): 20–25.

WATSON, T. L., and TABER, S. 1913. Geology of the titanium and apatite deposits of Virginia. *Virginia Geo. Survey Bull.* **3A**: 308 pp.

WELLER, Stuart. 1907. Notes on the geology of southern Calhoun County. *Illinois Geol. Survey Bull.* **4**: 219–233.

WILBUR, F. A. 1883. Apatite; marls. *U. S. Geol. Survey Mining Resources of U. S.*, **1882**: 521–526.

WOODRING, W. P., BRAMLETTE, M. N., and KEW, W. S. W. 1946. Geology and paleontology of the Palos Verde Hills, California. *U. S. Geol. Survey Profess. Paper* **207**: 145 pp.

CHAPTER XII

Technical and Economic Factors Influencing Phosphate Fertilizer Production in the United States

J. H. WALTHALL and E. C. HOUSTON

I. Introduction

The production of phosphate fertilizers is one of the oldest of the chemical industries. In addition to the technical and economic factors that influence industry in general, many special factors affect phosphate fertilizer production. Among these are the seasonal market; the variations in soils, crops, and climates which call for different kinds of fertilizers; and the diversified regulations with respect to marketing. Currently the industry is affected by several other factors, such as shortage of sulfuric acid, the rapid increase in the use of phosphate fertilizers, the goals set for marked expansion of fertilizer production, the interest in phosphate rock as a source of uranium, and the rapid growth of the fixed nitrogen industry. At no time has the phosphate industry been subjected to so many factors that tend to influence its scope and direction. The purpose of this paper is to discuss some of the technical and economic factors that are currently influencing the domestic production of phosphate fertilizers. It is hoped that by bringing together the various topics, many of which have been dealt with previously by others, certain interrelationships will be clarified and a better over-all perspective will be obtained.

II. Structure of the Industry

The structure of the phosphate fertilizer industry is outlined in the following.

1. Raw Materials

"Rock phosphate" is a general term covering the various phosphate minerals that serve as a source of practically all phosphate fertilizers. Most phosphate minerals occur in amorphous or microcrystalline form, which makes difficult their accurate mineralogical identification. Although it was formerly thought that tricalcium phosphate, $Ca_3(PO_4)_2$, was the principal phosphate compound present in rock phosphate,

this has been disproved. Recent studies have shown that the calcium phosphates present in rock phosphate belong to the apatite group which includes fluorapatite, $Ca_{10}F_2(PO_4)_6$, and hydroxyapatite, $Ca_{10}(OH)_2(PO_4)_6$.

In the United States rock phosphate is produced by some 35 companies and marketed according to P_2O_5 concentration and limits of impurities. Of the three producing regions, Florida accounts for about 75 per cent of the total, with Tennessee and the Idaho-Montana region sharing about equally in the production of the remainder. The rock phosphate in most deposits ranges from high to low grade, and from rock amenable to considerable beneficiation by known commercial methods to rock amenable to very little beneficiation. Often these different kinds of rock are found closely associated, in which cases economical operation requires the mining of both low-grade and high-grade rock. High-grade rock is preferred in the principal phosphate fertilizer processes. Recent improvements in phosphate ore dressing have resulted in raising the grade of commercial rock phosphate and compensate for the depletion of natural high-grade rock. Even the highest-grade concentrates are still far from being mineralogically pure materials, and it is doubtful whether pure minerals can ever be produced commercially from the materials that characterize domestic rock phosphates. In notable contrast are the crystalline apatites found in Europe. Modern phosphate ore dressing seldom results in the recovery of more than 70 per cent of the P_2O_5, which leaves considerable room for improvement.

Next in importance to rock phosphate as a raw material in phosphate fertilizer manufacture is sulfuric acid; about 35 per cent of the total domestic production goes into the manufacture of phosphate fertilizers. Sulfuric acid production is widely distributed geographically. A major portion is made in plants owned and operated by the fertilizer producers at or near the places where it is used. In these cases elemental sulfur from the Gulf Coast is the usual raw material. In 1950 the phosphate fertilizer industry produced about 70 per cent of the sulfuric acid that it used, and the remainder was purchased from nonfertilizer manufacturers. This subject is discussed further under Section III.

2. Ordinary Superphosphate

The principal process for making phosphate fertilizer was invented more than 100 years ago. It consists of mixing rock phosphate with sulfuric acid, followed by aging the mixture, whereby a dry, porous product known as "ordinary superphosphate" or "normal superphosphate" is obtained (Siems, 1951, p. 402). Ordinary superphosphate consists

essentially of monocalcium phosphate and calcium sulfate, with various impurities derived from the rock. The P_2O_5 content is usually between 16 and 24 per cent, depending on the composition of the rock and the proportion of rock to acid. The process was carried out in the early days by sprinkling the acid on the rock in open boxes while raking the mixture back and forth. The process has, over the years, become mechanized, although it remains empirical to a large degree owing to the nature of rock phosphate. Ordinary superphosphate currently accounts for about 77 per cent of all phosphate fertilizer production on the basis of P_2O_5 and excluding raw rock for direct application. It is seldom that a chemical process remains in such a dominant position for so long. The main reasons why superphosphate has held its position are the simplicity of the process, the widespread distribution of sulfuric acid, the excellent properties of the product, and established precedent.

In 1951 there were, according to Adams and co-workers (1952), about 200 plants making ordinary superphosphate, and these were distributed among 32 states. The wide decentralization of ordinary superphosphate manufacture is promoted, among other things, by the fact that it costs less to ship rock phosphate and sulfur than it does to ship superphosphate; not only does the rock carry a higher concentration of P_2O_5, it also travels at a lower freight rate. Over half of the 200 plants were totally or partially owned subsidiaries of companies engaged in rock phosphate production, having the advantage of integrated operations; and about 95 per cent of all plants utilized Florida rock phosphate. About 30 per cent of the plants were independent units. The capacity of individual plants ranged from about 20,000 to 500,000 tons of superphosphate per year, with capital investment averaging around $9 per annual ton (Abrahamsen, 1951). About half of the plants were served by coexisting plants for making sulfuric acid.

A major portion of the output of ordinary superphosphate is used in preparing mixed fertilizers, usually in subsidiary mixing plants, and some of it is marketed as straight phosphate fertilizer. Superphosphate serves an important function as a carrier for nitrogen in mixed fertilizers; this is discussed under Section V.

3. *Triple Superphosphate*

Instead of sulfuric acid, phosphoric acid can be mixed with rock phosphate. The product is essentially the same as ordinary superphosphate except for the virtual absence of calcium sulfate, which increases the P_2O_5 concentration to from 42 to 48 per cent, with an average of 46 per cent. Such material is known as "double superphosphate," "concentrated superphosphate," or "triple superphosphate" (Siems, 1951, p.

419). The first commercial production occurred in 1872 in Germany and around 1900 in the United States. Most of the phosphoric acid used for making triple superphosphate is made by the wet process (Siems, 1951, p. 412), in which rock phosphate is mixed with sufficient sulfuric acid to convert it into phosphoric acid and calcium sulfate. The calcium sulfate and insoluble impurities from the rock are filtered from the impure acid. Phosphoric acid is also made commercially by the electric furnace process discussed under Section IV. In 1950 about 20 per cent of the total production of triple superphosphate was made from

TABLE I

COMPARATIVE COSTS OF ORDINARY AND TRIPLE SUPERPHOSPHATE ESTIMATED FOR 200-MILE RADIUS OF CAIRO, ILLINOIS

	Dollars per ton of P_2O_5		*Per cent of total*
Ordinary superphosphate			
Phosphate rock, 3.06 tons at $5.35 f.o.b.	16.37		
Sulfur, 0.66 ton at $21.00 f.o.b.	13.86		
Total, raw materials, f.o.b.		30.23	21.6
Freight on rock, Bartow, Fla., to Cairo, Ill., 3.06 tons at $7.30	22.34		
Freight on sulfur, Port Sulphur, Louisiana, to Cairo, 0.66 ton at $6.30	4.16		
Freight on superphosphate, Cairo to point 200 miles distant, 5 tons at $5.00	25.00		
Total, freight costs		51.50	36.7
Manufacturing cost and profit, 5 tons at $8.20[a]	41.00		
Bagging cost, 5 tons at $3.50	17.50		
Total, processing		58.50	41.7
Total cost to retailer		140.23	100.0
Triple superphosphate			
Phosphate rock, 3.22 tons at $5.35 f.o.b.	17.22		
Sulfur, 0.69 ton at $21.00 f.o.b.	14.49		
Total, raw materials		31.71	27.0
Freight on sulfur, Port Sulphur to Bartow, Fla., 0.69 ton at $5.00	3.45		
Freight on triple superphosphate, Bartow to Cairo, 2.2 tons at $11.26	24.77		
Total, freight costs		28.22	24.1
Manufacturing cost and profit, 2.2 tons at $22.50[b]	49.50		
Bagging cost, 2.2 tons at $3.50	7.70		
Total, processing		57.20	48.9
Total cost to retailer		117.13	100.0

[a] Difference between raw materials cost and market price of ordinary superphosphate at Cairo.
[b] Difference between raw materials cost and market price of triple superphosphate at Bartow.

electric furnace acid. At present the triple superphosphate output accounts for around 15 per cent (P_2O_5 basis) of the total production of phosphate fertilizers.

In 1950 triple superphosphate was produced in nine plants (Adams *et al.*, 1952) distributed among seven states. These plants all had integrated production of phosphoric acid; seven used wet-process acid, one used electric furnace acid, and one used spent electric furnace acid. About 80 per cent of the total production of triple superphosphate came from Florida rock.

It is seldom that the total production of a phosphoric acid plant is used for triple superphosphate manufacture, and, of the thirteen plants making wet-process acid, only seven make triple superphosphate.

In many areas the delivered cost of triple superphosphate, per unit of P_2O_5, is less than the delivered cost of ordinary superphosphate, although the latter is less expensive to manufacture. The extent of such areas is broadened with increase in freight rates, which have recently advanced more rapidly than has the manufacturing cost differential between triple and ordinary superphosphate. An illustration of the relative costs of triple and ordinary superphosphate delivered in a selected midwestern area is shown in Table I. The same relationship could be shown for many other places. Not only does triple superphosphate frequently show an economic advantage over ordinary superphosphate, but also it is almost a necessity in the formulation of high-analysis mixed fertilizers. As a result there is a decided upward trend in the market for triple superphosphate.

4. Ammonium Phosphate and Basic Slag

Domestic manufacture of ammonium phosphate fertilizer is carried out by the Mathieson Chemical Corporation near Houston, Texas, which plant has been in operation since 1946. Ammonium phosphate also is made at Trail, British Columbia, and exported to the United States. The process used at Trail, as described by Atwell (1949), consists of ammoniating wet-process phosphoric acid, or a mixture of phosphoric and sulfuric acids, followed by evaporation, granulation, and drying. The most common grade is 16–20–0, which contains both ammonium phosphate and ammonium sulfate. Other grades include 11–48–0 and 13–39–0. The economics are closely related to the economics of wet-process phosphoric acid and triple superphosphate. In ammonium phosphate production the troublesome and expensive concentration of the wet-process acid required for triple superphosphate is avoided; evaporation is transferred to the much less troublesome ammonium phosphate solution. Also, production of the wet-process acid is

a less exacting operation, since an excess of sulfuric acid can be conveniently tolerated, and is sometimes purposely added, in ammonium phosphate manufacture. Ammonium phosphate does not require an aging step, whereas triple superphosphate does. A potential drawback of the process is that less P_2O_5 is produced, per ton of sulfuric acid, than in superphosphate manufacture.

In the production of steel by the basic open-hearth process, the use of an iron ore high in P_2O_5 results in the production of a slag containing about 10 per cent P_2O_5. Such slag, ground to 80 per cent through 100 mesh, is marketed under the name "basic slag" and has long been a popular fertilizer in this country and in Europe. Although the basic open-hearth process is widely used throughout the steel industry, production of basic slag fertilizer is limited to one southern mill. The P_2O_5 content of basic slag can be enriched by adding ferrophosphorus to the steel furnace, a practice followed in Europe but not in this country. Increased production of byproduct ferrophosphorus and rising demand for phosphate fertilizers may cause that practice to be adopted here.

5. *Semicommercial Processes*

Calcium metaphosphate fertilizer has been made on a semicommercial scale by the Tennessee Valley Authority since 1938. The process has been described by Yates and co-workers (1951). Since approximately 70 per cent of the P_2O_5 content of calcium metaphosphate is derived from elemental phosphorus, its economics are closely tied to the cost of phosphorus production, discussed under Section IV.

The fusion and partial defluorination of rock phosphate in a fuel-fired shaft furnace, followed by quenching the melt and grinding, result in the production of a phosphate fertilizer known as "fused tricalcium phosphate" (Hignett and Hubbuch, 1946). That material has been produced in a demonstration plant by the Tennessee Valley Authority since 1945. It contains 27 to 30 per cent P_2O_5, of which about 70 per cent is soluble in neutral ammonium citrate. The total P_2O_5 concentration is about 50 per cent greater than that of ordinary superphosphate and the material is not water-soluble, both factors being conducive to economy in distribution. The process is independent of sulfur and low-cost electric power and the requirements relative to the grade of rock are much less exacting than in most phosphate processes. Various kinds of fuel can be used including oil, natural gas, and powdered coal; this makes the process adaptable to the most economical fuel in any locality. Despite these strong advantages, the process is handicapped by the relatively low citrate solubility of the product as measured by the official test and the fact that its recommended field of use is somewhat re-

stricted. Because of its low rate of solubility, fused tricalcium phosphate is not recommended for short-season row crops, although extensive tests on pastures have shown it to be equal to superphosphate on a basis of total P_2O_5 on acid or neutral soils. (See Chapter VI.) If the product could be priced on the basis of its total P_2O_5 content, its cost would compare favorably with that of superphosphate, but priced on the basis of its citrate-soluble P_2O_5 it is uneconomical. That is an unfortunate situation because fused tricalcium phosphate is a very effective and potentially economical fertilizer in its recommended field. Changes in the fertilizer control laws of most states would be necessary, however, to remove the handicap.

A process by which phosphate fertilizer is produced by melting together a mixture of rock phosphate and olivine or serpentine in an electric furnace was developed through the pilot-plant stage by the Tennessee Valley Authority (Walthall and Bridger, 1943) and later put into semicommercial production by two western companies, although production has been subsequently discontinued by both. Moulton (1949) gives a description of the process as carried out by one of those companies. The product, known as "Thermophos" or "calcium-magnesium-phosphate," contains around 22 per cent P_2O_5, of which about 85 to 95 per cent is citrate-soluble, depending on fineness of grinding. Like fused tricalcium phosphate it is not a general-purpose fertilizer. The western location was chosen because of the proximity of olivine or serpentine and rock phosphate plus the availability of electric power and convertible war surplus equipment. However, the western location proved to be inauspicious because the product turned out to be ineffective on the alkaline soils that occur in much of the West. (See Chapter VI.) The process is currently in operation in Japan, where the product has proved highly effective on acidic soils that are deficient in phosphorus and magnesium.

III. The Sulfur Problem

As operated today the phosphate fertilizer industry is as dependent on sulfuric acid as on rock phosphate. Over 90 per cent of the phosphate fertilizer production is based on processes that use sulfuric acid, either directly, as in superphosphate, or indirectly, as in triple superphosphate or ammonium phosphate. Sulfuric acid is produced from several different raw materials, of which elemental sulfur is by far the most important. Prior to about 1910 elemental sulfur was relatively unimportant in comparison with "pyrites," a group term used to designate several iron sulfide minerals. By 1910, however, the domestic production of elemental sulfur by the Frasch process (Shearon and Pollard, 1950)

from deposits along the Gulf Coast had developed to the point where sulfur became the most economical raw material for sulfuric acid manufacture in most localities of the United States and abroad. Industry gradually turned from pyrites to sulfur, and by 1940 sulfur had displaced pyrites as the dominant raw material. There are three fundamental advantages of sulfur in comparison with pyrites: (1) a sulfuric acid plant that uses sulfur costs less to build, (2) a smaller scale of operation is economical, which fits into the pattern of decentralization of the phosphate industry, and (3) the concentration of sulfur is practically 100 per cent in commercial elemental sulfur as compared with 25 to 45 per cent in pyrites and 32 per cent maximum in sulfuric acid. Commercial elemental sulfur affords a much larger economical radius for shipment, and this is one of the principal factors that facilitated decentralization of the phosphate industry.

In 1947 the first serious indications of a sulfur shortage became evident to the users of sulfuric acid. By 1950 sulfur producers found it desirable to start allocations, and during 1950 and 1951 the situation received widespread publicity. Two basic factors are responsible for the shortage: (1) sulfur production capacity appears to have about reached its peak, further increases being hampered by depletion of reserves, and (2) demand for sulfur has increased continuously and has outstripped the capacity of the sulfur producers. At a time when the phosphate industry needs more sulfur in order to expand production of fertilizers, it is faced with difficulties in obtaining even enough sulfur to keep fertilizer production at present levels.

Exports have accounted for an appreciable proportion of domestic sulfur production. In 1940 exports amounted to 27 per cent of total production, and they amounted to 28 per cent in 1950. From 1940 to 1950 sulfur production increased by about 90 per cent and export tonnage increased in like ratio.

Since pyrites was formerly the principal raw material for sulfuric acid and a considerable proportion is still being made from pyrites, the possibilities of reconversion merit attention. Estimated reserves are quite large, but it is seldom that the use of pyrites is an attractive alternative. A pyrites acid plant costs more to build, as mentioned earlier, and the deposits of pyrites are generally remote from the fertilizer markets. Because sulfur is still being produced in sufficient quantities to supply a major portion of the industry, plants that use pyrites will have to compete with plants that use sulfur. There is always the possibility that discovery of new deposits of sulfur may abate the shortage. Such an eventuality is a threat to any investment in a pyrites acid plant, even

though such a plant could be converted readily to the use of sulfur. Despite the drawbacks, there probably is room for economical expansion in the use of pyrites as a source of sulfuric acid, especially if new plants are large enough so that the economies of large-scale operation can counteract the drawbacks.

Spent or impure sulfuric acid is obtained as a byproduct in several industries and has been used for some time in making ordinary superphosphate. The usual procedure is to use a mixture of spent acid and virgin acid. The sulfur shortage has increased the emphasis on such practice, although the shortage has also increased the emphasis on reuse by the primary producers. In 1950 less than 10 per cent of the acid consumed in the phosphate industry was spent acid.

IV. Electric Furnace Process

The production of elemental phosphorus by the reduction of charges of rock phosphate, coke, and silica in an electric furnace has been carried out commercially for over 40 years. The process has been described by Burt and Barber (1952) and a review of the industry has been made by Aall (1952). Domestic production of elemental phosphorus has more than doubled in the period 1946 to 1951, with seven producers in the field. Except for that produced by the Tennessee Valley Authority, very little elemental phosphorus goes into the manufacture of fertilizers because, until fairly recently, fertilizers could be made more cheaply by other processes. The sulfur shortage and other factors are, however, bringing electric furnace phosphorus into a competitive position in the fertilizer field.

Elemental phosphorus serves as an intermediate in the preparation of a wide variety of products, and subsequent processing depends on the kind of product to be made. Generally, the first step consists of converting the elemental phosphorus to phosphoric acid. Since elemental phosphorus represents the ultimate with regard to concentration, it is frequently shipped for considerable distances in tank cars and converted to acid at locations closer to the market for the final products. Phosphoric acid is produced by burning elemental phosphorus to form P_2O_5, which then is cooled and contacted with sprays of water to form phosphoric acid, H_3PO_4.

Phosphoric acid from elemental phosphorus is considerably purer than that produced by the wet process, and therefore can be used wherever wet-process acid is suitable, as in triple superphosphate or ammonium phosphate production. The superior purity of electric furnace acid increases the grade of triple superphosphate, but otherwise

confers no significant technical advantage over wet-process acid in fertilizer manufacture. The high purity of the acid is frequently a decisive asset in other manufactures.

From the standpoint of raw materials the electric furnace process has two distinct advantages over the wet process. One advantage is an independence of sulfuric acid, and another is a much less exacting requirement as to the grade of rock phosphate. Although domestic rock phosphate reserves are enormous, a large proportion of these reserves exist as low-grade ores which cannot be economically beneficiated to a quality suitable for use in making ordinary superphosphate or triple superphosphate by the wet process, but which can be produced in grades suitable for the electric furnace process.

The major expense in the electric furnace process, other than the cost of rock phosphate, is the cost of electric power. In comparison, the major expenses in wet-process phosphates, other than the cost of rock phosphate, is the cost of sulfuric acid.

In making triple superphosphate from electric furnace acid each ton of P_2O_5 in the product requires about 4200 kw.-hr. of power. In comparison, about 2.40 short tons of 60° Bé. sulfuric acid are required for each ton of P_2O_5 in wet-process triple superphosphate. Differences in manufacturing costs between the two processes, exclusive of the cost of power and acid, would add about $6 to the electric furnace process per ton of P_2O_5 in the product. A rough comparison of the cost of power with the cost of 60° Bé. sulfuric acid is therefore shown in the equation:

$$x = \frac{4200y}{2.40} + 6.00$$

in which x = cost per ton of 60° Bé. sulfuric acid
and y = cost per kw.-hr. for power

If, for example, it is desired to find the unit cost of sulfuric acid that is equivalent to power that costs 5 mills per kw.-hr., that value is substituted for "y" in the equation, and

$$x = \frac{4200 \times 0.005}{2.40} + 6.00$$

or $14.75 per ton of 60° Bé. sulfuric acid. It should be realized that in the equation the $6 "constant" applies to typical conditions, and may vary appreciably in specific cases.

The economics of electric furnace fertilizer are strengthened by the feasibility of diverting a portion of the phosphorus to the production of detergents or other nonfertilizer products. So long as those markets are unsaturated, however, there will be no financial incentive for using phosphorus to make fertilizers, which are lower-valued commodities.

V. Nitric Phosphate Processes

The use of nitric instead of sulfuric acid for manufacturing phosphate fertilizers has been carried out commercially in Europe for over 20 years. Recently, conditions in this country have become favorable to such processes (Hignett, 1951). The sulfur shortage and a marked in-

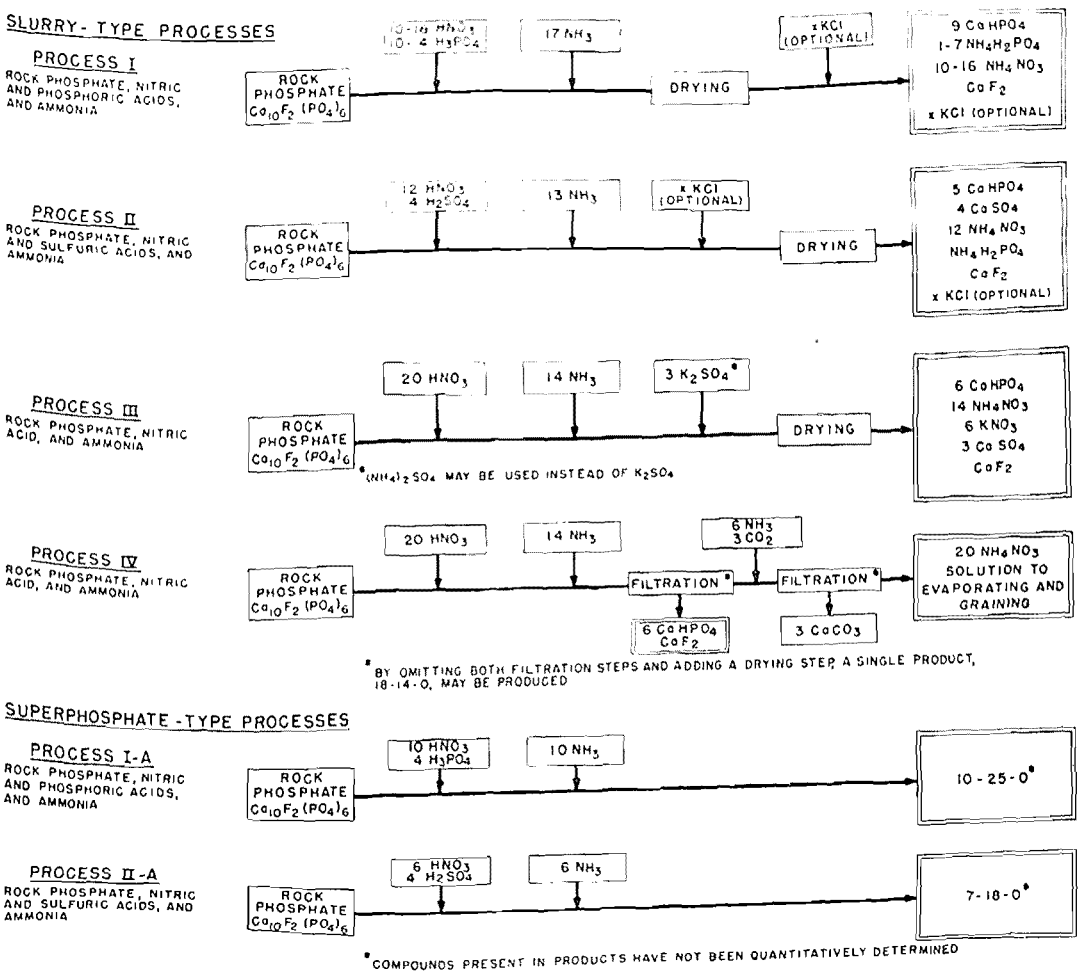


FIG. 1. Nitric phosphate processes.

crease in production and decrease in cost of fixed nitrogen have stimulated domestic interest in nitric phosphate processes. Figure 1 shows diagrammatic flow charts for six processes that use nitric acid as the principal acidulant in treating rock phosphate. The slurry-type processes, Fig. 1, are those in which the mixtures of rock and acid are in

fluid state, as contrasted with the superphosphate-type processes in which they are in friable state like superphosphate. Pilot-plant studies of processes I and II have been reported by Houston *et al.* (1951) and Striplin *et al.* (1952). Similar studies of process II-A have been reported by McKnight *et al.* (1952).

The principal advantage in the use of nitric acid for phosphate fertilizer production is economic, owing in part to economies in the use of

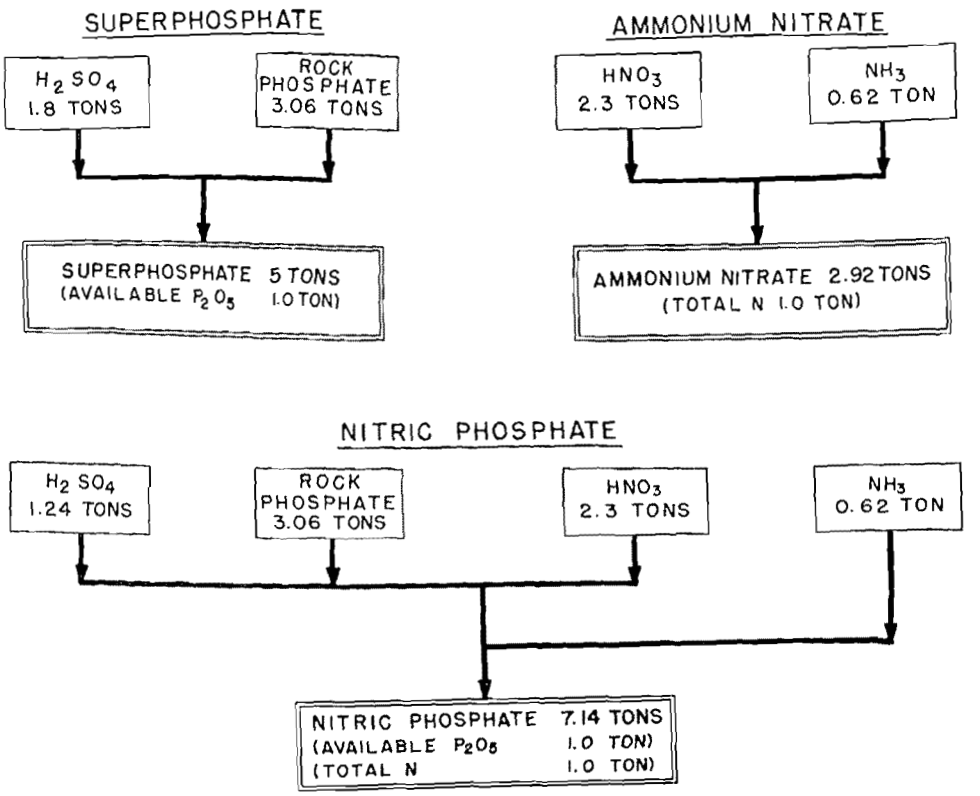


FIG. 2. Raw material requirements: nitric phosphate, superphosphate, and ammonium nitrate.

raw materials, as illustrated in Fig. 2, which compares process II (Fig. 1) with superphosphate and ammonium nitrate. The manufacture of 1 ton of available P_2O_5 in the form of nitric phosphate is shown, Fig. 2, to require 31 per cent less sulfuric acid than is required to produce the same amount of P_2O_5 in the form of superphosphate. Greater savings in sulfuric acid are obtainable by using different proportions of rock and acid, but the conditions shown in Fig. 2 are better for illustrative purposes. The nitric acid and ammonia make 1 ton of fertilizer nitrogen,

regardless of whether they are used in the nitric phosphate process or in the ammonium nitrate process. Wherever ammonium nitrate fertilizer production is economical, which covers many locations, the cost of both nitric acid and ammonia used in nitric phosphate is chargeable to fertilizer nitrogen rather than to P_2O_5 production.

Another economic advantage of nitric phosphate processes is the considerably greater market value of compound fertilizers as compared with separate phosphate and nitrate fertilizers due, in part, to the expenses of formulation and mixing. The nitric phosphate processes afford an opportunity for adding potash during processing to make a product that contains all three of the major plant foods in a homogeneous, nonsegregating form.

Solid ammonium nitrate has, because of its low price, become popular as a fertilizer despite its unfavorable hygroscopicity and explosion hazard. Nitric phosphate processes, in effect, put ammonium nitrate in a form much more favorable for fertilizer use. The phosphatic constituent is principally dicalcium phosphate, a nonhygroscopic thermally stable compound that by its diluent action makes the ammonium nitrate less likely to cake and eliminates the hazard of explosion. Nitric phosphates have a relatively high ratio of N to P_2O_5, which is frequently desirable but difficult or costly to attain by means of the more conventional methods.

Field tests have been run on experimentally produced nitric phosphates of the compositions shown in Table II, and the results have been reported by Rogers (1951) (see also Chapter VII).

TABLE II

COMPOSITION OF NITRIC PHOSPHATES PRODUCED BY TENNESSEE VALLEY AUTHORITY[a]

	Composition, per cent							
		P_2O_5						
Nominal grade	*N total*	*Total*	*Citrate-soluble*	*Water-soluble*	K_2O	*CaO*	SO_3	*Net acidity, pounds $CaCO_3$/ton*
14–14–14	15.3	14.3	14.0	2.0	15.2	11.1	...	495
17–22–0	17.5	22.2	21.9	1.6	....	17.1	.	350
12–32–0	12.4	34.6	31.2	14.5	....	19.8	...	505
11–11–11	11.1	11.7	11.3	1.8	11.7	16.6	9.5	350

[a] Used in field tests reported by Rogers (1951).

In evaluating a new process, the usual standard of comparison is the process the new one is intended to replace. In the case of nitric phosphate processes, however, there is no single standard process for com-

parison, because those processes are, essentially, combinations of several separate processes including superphosphate manufacture, ammonium nitrate manufacture, formulation and mixing, granulation, and sometimes wet-process phosphoric acid manufacture. Since manufacture of ordinary superphosphate is the most common phosphate process, it has sometimes been compared illogically with nitric phosphate processes.

The use of nitric phosphate processes in this country would mean an innovation in the existing structure of the fertilizer industry. It is therefore appropriate to consider certain interrelationships now in effect between the nitrogen industry and the phosphate industry.

In the production of fixed nitrogen the first product to be made is ammonia, which can be processed to make nitric acid and finally ammonium nitrate. Since ammonia requires the least processing, it is the least expensive of the three materials. It is also the most concentrated with regard to nitrogen and is relatively inexpensive to ship. Nitric acid, obtained by oxidation of ammonia, is the most expensive of the three materials as well as the least concentrated form of nitrogen and the most expensive to ship. Nitric acid is therefore usually converted, at the place where it is made, into other products more convenient to handle, such as ammonium nitrate or sodium nitrate. Ammonium nitrate is made from nitric acid and ammonia and in price is somewhere between the two. It is first obtained in the form of an aqueous solution which may be processed further to prepare the dry solid.

In 1951 synthetic ammonia was produced in 21 plants that were distributed among 12 states. The total production of synthetic ammonia for the 12-month period ended June 30, 1951, amounted to 1,659,353 short tons, of which about 65 per cent went into fertilizers, in the following forms:

Material	*Per cent of total, N basis*
Ammoniating solutions	36.6
Ammonium nitrate, solid	21.7
Ammonium sulfate	15.8
Anhydrous ammonia, direct application	11.9
Ammonium phosphate, urea, sodium nitrate	8.7
Anhydrous ammonia for ammoniation	5.3
	100.0

As shown in the foregoing tabulation, a major portion of the fixed nitrogen fertilizer material is produced in the form of ammoniating solutions which are not consumer products but are intermediate materials used by the phosphate fertilizer industry.

The treatment of superphosphate with ammonia is a widespread

practice that serves a double purpose: (1) ammonia acts as a conditioner for superphosphate, and (2) the ammonia is converted into a solid stable form convenient for fertilizer use. The principal reactions that occur between superphosphate and ammonia are shown in the following equations:

$$Ca(H_2PO_4)_2{\cdot}H_2O + NH_3 = CaHPO_4 + NH_4H_2PO_4 + H_2O$$
$$NH_4H_2PO_4 + CaSO_4 + NH_3 = CaHPO_4 + (NH_4)_2SO_4$$

Although anhydrous ammonia is used to some extent in the ammoniation of superphosphate, most of the ammonia for that use comes from aqueous solutions that contain ammonium nitrate (or sometimes urea) as well as ammonium hydroxide. Several such solutions are on the market. About 50 per cent of the nitrogen content of ammoniating solutions is in the form of free ammonia. Shipped in tank cars to the superphosphate plants throughout the country, they serve to supply, almost exclusively, the first 2 to 4 per cent of the nitrogen in mixed fertilizers. More would be added except for an undesirable side reaction that leads to the formation of fluorapatite (MacIntire and Hardin, 1940; Hecht *et al.*, 1952). Because of the ceiling on the proportion of nitrogen that can be added in the form of ammoniating solutions, it is necessary in current practice to use higher-cost nitrogen, such as ammonium sulfate or sodium nitrate, whenever it is desired to increase the nitrogen above 3 parts of N to 10 parts of P_2O_5 in mixed fertilizer.

The production of ammonia for fertilizer use involves the problem of off-season storage. Although all parts of the fertilizer industry are confronted with that problem, it is particularly serious in the case of ammonia. An ammonia plant, for economy, must operate continuously on a year-round basis. Anhydrous ammonia can be stored only in pressure vessels, and the capital cost of such vessels is so high that it is almost equal per ton to the capital cost of ammonia manufacturing facilities. Solution of the problem lies in converting ammonia into more conveniently storable forms such as ammonium nitrate, urea, ammonium sulfate, ammonium phosphate, ammoniated superphosphate, and, to some extent, ammoniating solutions. Plant capacity for the conversion of ammonia into ammonium nitrate or urea is currently far short of capacity for ammonia production, although plants now being built will help to close the gap. Ammonium sulfate production is beset with the sulfur shortage since the process now in use in this country requires sulfuric acid, although a commercial process is available that does not require acid (Higson, 1951). With the exception of the ammoniation of superphosphate, all methods for converting ammonia into solid forms increase the unit cost of the nitrogen.

The interdependence of superphosphate and ammonia is apparent

from the foregoing discussion. At present, however, there is little integration of production; few manufacturers make both materials. Although better integration might be mutually beneficial, it is obviously not essential in the present status of the industry. In contrast, integration of nitrogen and phosphate facilities is prerequisite for nitric phosphate production, widely advocated as a sulfur conservation measure. Because they represent the younger and more flexible of the two groups, the fixed nitrogen producers will probably take the initiative with regard to that integration, although they lack the well-established fertilizer distribution system of the phosphate producers.

VI. Uranium

The effects of an unforeseeable external development on the phosphate industry are illustrated by the case of uranium. The development of atomic energy is dependent on a supply of uranium, a rare element. That situation has stimulated a search for uranium. In the course of that search uranium was found to occur in small percentages in certain rock phosphates of Florida and of the West (Wimpfen, 1951). It was found also that phosphoric acid prepared by the wet process from uranium-bearing rock phosphates contains most of the uranium in a form amenable to recovery before the acid is used to make either triple superphosphate or ammonium phosphate. Only about 10 per cent of the current production of phosphate fertilizers is made from phosphoric acid, and it would be more desirable to recover uranium from the principal product, ordinary superphosphate, but that is still an unsolved problem. There is currently no alternative to increasing the production of phosphoric acid and the fertilizers made from it. Such an increase would present several problems. In the first place, phosphoric acid manufacture requires more sulfuric acid per ton of product P_2O_5 than does superphosphate, thereby aggravating the sulfur shortage. The economical utilization of an increased production of phosphoric acid is also a problem. The construction of new triple superphosphate or ammonium phosphate plants adjacent to the phosphoric acid plants would duplicate existing facilities that might have to operate at reduced capacity as a result of the curtailment of sulfuric acid supply. A possible expedient would be to ship the phosphoric acid to existing superphosphate plants, where the acid would be used to make either triple superphosphate or "enriched superphosphate," the latter being made from mixed sulfuric and phosphoric acids. One drawback to such an expedient is the high cost of shipping phosphoric acid, as compared with shipping either rock phosphate or superphosphate. As a counteracting

factor, present plants would be utilized and the present fertilizer mixing and distribution system would not be disrupted.

Recovery of uranium from nitric phosphate processes is an interesting possibility that is being investigated.

VII. Particle Size, Caking, Drillability, and Granulation

A major factor in the evaluation of a phosphate as a plant food is the rate at which it dissolves in the soil solution. Rate of dissolution is dependent on several factors, of which chemical composition and particle size can be controlled by the manufacturer. Chemical composition is relatively stable for any given set of process conditions and will not be discussed here. Particle size, however, is amenable to a wide adjustment without major changes in processing operations.

The rate of dissolution of any material increases with decrease in particle size, since dissolution is a surface phenomenon and the amount of surface increases with fineness of the particles. The rate of dissolution of the quickly soluble phosphates such as monocalcium phosphate or ammonium phosphate is so rapid that, from the standpoint of solubility as measured by the laboratory test, particle size is immaterial. The less soluble phosphates such as calcium metaphosphate, fused tricalcium phosphate, or calcium-magnesium phosphate require fine grinding to obtain adequate rates of dissolution. Some furnace products are not only composed of slowly soluble phosphates, but these may sometimes be encased by insoluble glassy materials, in which cases fine grinding is needed to liberate the phosphate. There are two practical considerations that limit fineness in grinding: (1) cost, and (2) dustiness which is objectionable in handling the material.

Certain phosphates, such as fluorapatite, are so insoluble that even the finest grinding will not bring the solubility up to acceptable levels, as measured by the official laboratory test. Although solubility is a controlling factor in selecting the particle size of the less soluble phosphates, other factors enter into the decision as to particle size of the more soluble phosphates, and these factors are discussed in the following pages.

1. Caking and Drillability

Fertilizers become caked during storage because of recurrent changes in humidity or temperature or both. Caking can also occur from chemical reactions, for example, between superphosphate and ammonium sulfate. When the relative humidity is high and the material is exposed to the atmosphere, a film of moisture is absorbed on the sur-

face of the particles and dissolves enough salt (in the case of water-soluble materials) to form a saturated solution. If the humidity or the temperature becomes lower, crystals are deposited from the solution and act as a cementing agent to bond the particles together. The severity of caking is affected by the size of the particles. Large, closely sized particles form loose friable aggregates that break up during normal handling, whereas fine particles form hard dense aggregates that are troublesome to handle (Mehring *et al.*, 1935). In the case of a material completely shielded from atmospheric moisture, caking can still occur, as a result of changes in atmospheric temperature that affect the solubility of salts in the residual moisture. A perfectly dry material packaged in a moistureproof container should remain uncaked indefinitely, regardless of particle size, hygroscopicity, and atmospheric conditions, except for materials that undergo changes in crystal form, such as ammonium nitrate. Similarly, a free-flowing material that contains some residual moisture should remain uncaked when stored in a moistureproof container under constant-temperature conditions, irrespective of particle size or hygroscopicity. Even the best bags fail, however, to provide a perfect seal against moisture. Furthermore, it is not commercially feasible to prepare completely dry fertilizers or to store fertilizers at constant temperatures. The foregoing discussion is intended however, to bring out some fundamentals of caking.

Solid fertilizers are usually applied to the soil by means of a mechanical dry feeder, or "drill," of which there are several designs on the market. The efficient utilization of a fertilizer depends, to a large degree, on proper placement in the soil, which in turn depends both on the machine and on the flow characteristics or "drillability" of the fertilizer.

The flow characteristics of solids are influenced by the size of the particles, and by their mositure content and shape. Mehring and coworkers (1935) conducted tests on the flow characteristics of solid fertilizers and found that, from the standpoint of drillability, 20 to 80 mesh is the most satisfactory range of particle size. They found that as the moisture content was increased, the limiting size for gravity flow was increased. Under their test conditions material as fine as 300 mesh would not flow even when drier than usually encountered commercially, whereas the same material in the form of 20- to 30-mesh grains would flow, even when very damp.

2. Granulation

Many fertilizer manufacturers have turned to granulation as a means for improving the storage characteristics and drillability of their

products. A typical process consists of moistening fine material while it is being tumbled in a rotating drum, causing agglomeration of the particles into pellets. The damp, soft pellets are next dried to harden them, after which they are screened to the desired size. Hardesty and Clark (1951) have described the principal processes in use. At present there is no clear criterion for differentiating between granular and nongranular fertilizer. The former may range from material that has been subjected merely to a sizing operation to remove lumps and fines to material that consists of closely sized spherical particles. Nongranular fertilizer does not necessarily contain excessive proportions of fines. Some manufacturers intentionally leave in a portion of the fines instead of producing only very closely sized large particles. Such material is sometimes called "free-flowing fertilizer," reserving the term "granulated fertilizer" for the more closely sized product. In tests with nitric phosphates reported by Rogers (1951), indications are that a certain proportion of fines may sometimes give greater crop responses in comparison with material comprised exclusively of very closely sized large granules. Granulation affects placement, which is one of the major variables in the application of fertilizers. The best particle size from the standpoint of reduction of caking and improvement of drillability may not necessarily be the best particle size from the standpoint of crop response (Mehring *et al.*, 1935; Rogers, 1951). Physical condition is readily observable, and there is a distinct sales appeal in large, closely sized granules. The agronomic effectiveness of granulation is not evaluated so readily, however.

VIII. Western Phosphates

For many years phosphate fertilizers have been produced on a limited scale in Montana and British Columbia; rock from the Idaho-Montana region and byproduct sulfuric acid from smelter operations are used. Geographically the western rock phosphates are distant from the principal markets for fertilizer; this fact has held back their development. There are, however, large agricultural areas currently served by Florida or Tennessee phosphates that, potentially, could be served more economically by western phosphates. Since the reserves of western rock exceed those of Tennessee and Florida, greater use of the western phosphates is desirable from a standpoint of conservation.

Recently several factors have made the situation more favorable for western production of phosphate fertilizers. The fertilizer market has increased about sevenfold in the western North Central States from 1941 to 1951, and much of that region lies within the economical radius for western phosphates. The Tennessee phosphate field, which is the

closest competitor for that market, is becoming exhausted, particularly with regard to the high-grade rock preferred for making superphosphate. In the past 5 years there has been a phenomenal growth of electric furnace phosphorus production in several localities, including the West. Although that production is primarily for nonfertilizer materials, it brings with it an increase in scale of production of western rock phosphate. Larger-scale mining of western rock will lead to more complete data on rock composition and mining costs. In addition, large-scale mining of furnace-grade rock should lower the cost of mining the associated high-grade rock suitable for wet-process phosphate fertilizer production. The sulfur shortage is less serious in the West than in most other regions, because of the availability of byproduct sulfuric acid from western smelters, the availability of pyrites, sometimes in the form of tailing from metallurgical processes, and the potentialities of recovering sulfur from western natural gas. Possibility of the use of western deposits of trona, a natural bicarbonate of soda, has aroused interest as to the utility of the Rhenania process used in Europe, which comprises calcination of a mixture of rock phosphate and sodium carbonate.

With regard to processes, the long shipment required to bring western phosphates to the larger markets favors products having high concentrations of plant food, such as concentrated superphosphate, calcium metaphosphate, and ammonium phosphate. Shipment of western phosphorus in elemental form for conversion into phosphoric acid for fertilizer production nearer the consumer will no doubt receive consideration. Development of a standard "packaged" plant for making phosphoric acid from phosphorus, comparable to present plants for making sulfuric acid economically on a relatively small scale, would be helpful in promoting the shipment of western phosphorus for fertilizer use. The western phosphate field is in a stage of rapid industrial expansion. Although most of the expansion is for products other than fertilizers, there are indications that the region will play an increasingly important part in the phosphate fertilizer industry (see Chapter XI).

IX. Byproducts

The phosphate industry produces numerous byproducts, some of which are marketable and add to the income from the manufacturing operations, whereas others constitute atmospheric or stream pollutants unless special provision is made to render them innocuous. It is not logical to designate these latter materials as "wastes," since the term implies that they are without value. Although presently without value,

they may well become valuable at some later time, either through the development of new uses or better recovery processes.

1. Fluorine

All commercial domestic rock phosphates contain fluorine, the percentages ranging from about 3 to 4, and generally in excess of the stoichiometric requirement for fluorapatite, $Ca_{10}F_2(PO_4)_6$. In the manufacture of superphosphate 20 to 40 per cent of the fluorine is driven off, principally in the form of silicon tetrafluoride. The exact proportion volatilized depends upon the kind of rock as well as on the processing conditions (Siems, 1951, p. 406). In the various furnace processes the fluorine is driven off, principally in the form of hydrogen fluoride (Hignett and Siegel, 1949). That compound and silicon tetrafluoride are atmospheric pollutants that are harmful, even in relatively low concentrations, to both plant and animal life.

In 1951, according to Adams *et al.* (1952), sodium fluosilicate was produced at nine phosphate plants, potassium fluosilicate at four, zinc fluosilicate and magnesium fluosilicate at three plants each, ammonium fluosilicate at two, hydrofluosilicic acid at two plants, and sodium fluoride at one. In some plants the fluorides are merely scrubbed from the effluent gases, without recovery of marketable compounds.

Industrial uses for fluorine and fluorine compounds in metallurgy, petroleum refining, insecticides, plastics, and other fields are steadily expanding, although fluorspar, the principal raw material, is limited in extent. Rock phosphate is the most important alternative source of fluorine, the fluorine content of rock phosphate reserves exceeding that of the fluorspar reserves by more than a hundredfold. The volatilization of fluorine in domestic phosphate processes is estimated to amount to about 70,000 tons per year (Hignett and Siegel, 1949) as compared with 15,000 to 20,000 tons recovered in marketable forms (Adams *et al.*, 1952).

2. Phosphate Tailing

Rock phosphate occurs, in the Florida and Tennessee deposits, in the form of particles of apatite that are embedded in clay, much of which is colloidal. The preparation of the rock phosphate for commercial use includes a separation of the apatite from the clay by a system of washing and classification. The clay fraction constitutes a tailing, or waste, which is produced in the form of a dilute and stable suspension, quite resistant to dewatering. The disposal of the tailing is a difficult problem because of its resistance to dewatering and because of the large volumes

produced. Lagoons covering many acres at each plant are generally provided for impounding the tailing. Despite these facilities, the cost of which is often appreciable, much of the tailing finds its way into streams and wells, giving the water a muddy character.

3. *Vanadium*

Certain western rock phosphates contain vanadium, an element used in making special steels. The Anaconda Copper Mining Company has, since 1941, recovered vanadium as a byproduct of its phosphate fertilizer operations in Montana. Their process, described by Banning and Rasmussen (1951), is carried out in connection with the manufacture of wet-process phosphoric acid from rock phosphate containing about 0.25 per cent V_2O_5. The vanadium is separated from the acid by special treatment, and the acid is subsequently used to make triple superphosphate. When vanadium-bearing rock phosphate is used in the electric furnace process described under Section IV, the resultant ferrophosphorus contains most of the vanadium. The recent expansion in the electric furnace process in the West and the scarcity and importance of vanadium have stimulated research on processes to effect recovery of vanadium from ferrophosphorus (Banning and Rasmussen, 1951).

4. *Other Byproducts*

In the manufacture of wet-process phosphoric acid an impure calcium sulfate is a major byproduct, and large piles of that material have accumulated. The sulfur shortage has aroused interest in the use of such material as a source of sulfuric acid. A workable process is available for making sulfuric acid from calcium sulfate, but its utility is restricted by the need for making cement as a coproduct. In another process, calcium sulfate is used for making ammonium sulfate. In both processes, however, calcium sulfate in the form of mineral gypsum or anhydrite is generally preferred to byproduct calcium sulfate because of troublesome impurities in the latter material. In fact, one British plant making ammonium sulfate from calcium sulfate (Higson, 1951) operates with mineral anhydrite despite the presence of a large waste pile of byproduct calcium sulfate at the same plant.

In the use of wet-process phosphoric acid for the manufacture of sodium phosphates, the acid is subjected to a purification step that results in the production of a filter cake which is dried and sold for use as a conditioner for mixed fertilizers. That material, marketed under various names including Hy-Grade Neutral Phosphate and Tri-Product, contains about 40 per cent P_2O_5, which is practically all citrate-

soluble. Other constituents include CaO, 14 to 17 per cent; Al_2O_3 and Fe_2O_3, about 7 per cent each; and Na_2O, 11 to 22 per cent (Hill, 1952).

The production of phosphorus by the electric furnace process, as described under Section IV, gives rise to two byproducts useful in agriculture. One of these, calcium silicate slag, is a material that has been studied intensively and proved useful for the liming of acid soils (MacIntire *et al.*, 1945). The second byproduct having agricultural significance is a dust from the electrostatic precipitators, called "potash-phosphate ash," which contains typically 28 per cent P_2O_5 and 16 per cent K_2O. After agglomeration it is suitable for use as fertilizer. A third byproduct of electric furnace phosphorus is ferrophosphorus containing 18 to 25 per cent P. Ferrophosphorus is used by the foundry and steel industry but that market is limited and ferrophosphorus production has frequently exceeded demand. The byproduct carbon monoxide from the electric furnace is useful as a fuel in preparing the furnace charge, although the gas carries traces of phosphorus that are difficult to remove, making it unsuitable for use as fuel in steam boilers or other power-generating equipment.

References

Aall, C. H. 1952. The American phosphorus industry. *Ind. Eng. Chem.* **44**: 1520–1525.

Abrahamsen, M. A. 1951. Manufacturing costs as reported for cooperative fertilizer plants in the North Central States (1949). *U. S. Dept. Agr., Farm Credit Admin. Special Rept.* **218**.

Adams, J. R., Tremearne, T. H., Jacob, K. D., and Porter, L. G. 1952. Survey of the superphosphate and wet-process phosphoric acid industries in the United States in 1950 and 1951. U. S. Department of Agriculture, unnumbered report, May 14.

Atwell, J. 1949. Phosphate processes at Trail, B. C. *Ind. Eng. Chem.* **41**: 1318–1324.

Banning, L. H., and Rasmussen, R. T. C. 1951. Processes for recovering vanadium from western phosphates. *U. S. Bur. Mines Rept. Invest.* **4822**.

Burt, R. B., and Barber, J. C. 1952. Production of elemental phosphorus by the electric-furnace method. *Chem. Eng. Rept.* **3**. Tennessee Valley Authority, Knoxville, Tennessee.

Hardesty, J. O., and Clark, K. G. 1951. Granulation of fertilizers. *Agr. Chemicals* **6**(1): 34–38, 95, 97.

Hecht, W. J., Worthington, E. A., Crittenden, E. D., and Northrup, M. A. 1952. Citrate insoluble residue from an ammoniated superphosphate. *Ind. Eng. Chem.* **44**: 1119–1123.

Hignett, T. P. 1951. Nitric acidulation of rock phosphate. *Chem. Eng.* **58**(5): 166–169.

Hignett, T. P., and Hubbuch, T. N. 1946. Fused tricalcium phosphate. *Ind. Eng. Chem.* **38**: 1208–1217.

Hignett, T. P., and Siegel, M. R. 1949. Recovery of fluorine from stack gases. *Ind. Eng. Chem.* **41**: 2493–2498.

HIGSON, G. I. 1951. Ammonium sulfate from anhydrite. *Chemistry & Industry* **36**: 750–754.

HILL, W. L. 1952. Elemental phosphorus and phosphoric acid in fertilizer industry. *Ind. Eng. Chem.* **44**: 1526–1531.

HOUSTON, E. C., HIGNETT, T. P., and DUNN, R. E. 1951. Compound fertilizers from rock phosphate, nitric and phosphoric acids, and ammonia. *Ind. Eng. Chem.* **43**: 2413–2418.

MACINTIRE, W. H., WINTERBERG, S. H., and CLEMENTS, L. B. 1945. Calcium silicate materials: their distinctive behavior and liming effectiveness as registered by plant response and soil pH. *Soil Sci. Soc. Amer. Proc.* **10**: 71–80.

MACINTIRE, W. H., and HARDIN, L. J. 1940. Absence of reversion in ammoniated and limed superphosphates of low fluorine content. *J. Assoc. Offic. Agr. Chemists* **23**: 388–398.

MCKNIGHT, DAVID, ANDERSON, J. F., JR., STRIPLIN, M. M., JR., and HIGNETT, T. P. 1953. Superphosphate manufacture: partial replacement of sulfuric acid with nitric acid. *J. Agricultural and Food Chem.* **1**: 162–166.

MEHRING, A. L., WHITE, L. M., ROSS, W. H., and ADAMS, J. E. 1935. Effects of particle size on the properties and efficiency of fertilizers. *U. S. Dept. Agr. Tech. Bull.* **485**.

MOULTON, R. W. 1949. Electric furnace fertilizers: Ca-Mg-phosphate. *Chem. Eng.* **56**(7): 102–104.

ROGERS, H. T. 1951. Crop response to nitraphosphate fertilizers. *Agron. J.* **43**: 468–476.

SHEARON, W. H., JR., and POLLARD, J. H. 1950. Modern sulfur mining. *Ind. Eng. Chem.* **42**: 2188–2198.

SIEMS, H. B. 1951. Fertilizers. "Encyclopedia of Chemical Technology." Vol. 6, pp. 376–452, Interscience Encyclopedia, New York.

STRIPLIN, M. M., JR., MCKNIGHT, D., and HIGNETT, T. P. 1952. Compound fertilizers from rock phosphate, nitric and sulfuric acids, and ammonia. *Ind. Eng. Chem.* **44**: 236–242.

WALTHALL, J. H., and BRIDGER, G. L. 1943. Fertilizer by fusion of rock phosphate with olivine. *Ind. Eng. Chem.* **35**: 774–777.

WIMPFEN, S. P. 1951. Uranium from phosphate rock (a paper presented at the Natl. Fertilizer Assoc., Atlanta, November 14). Summarized in *Chem. Eng. News* **29**: 5112.

YATES, L. D., ROY, L. F., and MELINE, R. S. 1951. Improved fertilizer plant design. *Chem. Eng.* **58**(6): 135–137.

CHAPTER XIII

Phosphorus Status and Requirements of Soils in the United States

F. W. PARKER

I. Introduction

The nation's phosphorus resources may be classified under two broad categories, the phosphorus in the soil and deposits of phosphatic ores. The adequacy of the former for crop production determines the need for processing the latter into fertilizers. Thorough knowledge of the amount and condition of phosphorus in the virgin soils of the United States would provide a logical base for consideration of phosphorus fertilizer requirements for different crops and farming systems. Fortunately, the production of phosphate fertilizers to meet agricultural requirements did not await the development of such data. As the data became available, however, they helped to explain, as well as guide, the use of phosphatic fertilizers. Even at this relatively late date a thorough knowledge of phosphorus in virgin soils would be very useful to agriculture and the fertilizer industry.

The phosphorus status of soils may be greatly altered by management practices. Changes of tenfold or more in the capacity of a soil to supply phosphorus to crops are not uncommon. These changes are produced by a variety of practices, including the use of fertilizers, farm manures, liming, cropping, and water management. Additional information on the nature and magnitude of these changes is essential to an accurate estimation of phosphorus fertilizer requirements and to the efficient use of fertilizers.

In this chapter will be considered:

1. The phosphorus status of the virgin soils of the United States and the influence of various factors of soil genesis on the phosphorus status of soils.

2. The influence of various soil management practices on the phosphorus status of soils.

3. Trends in the phosphorus fertility status of soils of the United States.

4. Our requirements for phosphate fertilizers in the years ahead.

First, it may be well to define at least one term—the phosphorus

fertility status of soils. For the purpose of this discussion it means the capacity of the soil to supply phosphorus to a crop when other nutrient and environmental factors are not limiting growth. Obviously, if fertility status were to be expressed by a single value, the crop and other conditions of making the determination would have to be defined and standardized. We have not had a dependable method for determining the phosphorus fertility status that could be used on all soils. The *A* value method (Fried and Dean, 1952; Dean, 1952) may prove to be better than any other single measurement. (See Chapter II.) Even if that should be the case, it would still be desirable to have additional data on the quantity and forms of soil phosphorus. The ideal situation would be to have the following information on the various horizons of the soil profile:

1. Total phosphorus.
   a. Organic.
   b. Inorganic.
2. *A* value.
3. Phosphorus extractable by one or more chemical methods.

Such data on a given soil are comparatively rare. The discussion of phosphorus fertility status, therefore, must be based on more limited data.

II. Phosphorus Status of Virgin Soils

Total phosphorus content is the only available basis on which we can evaluate the phosphorus fertility of large numbers of virgin soils. It serves as an index of phosphorus reserves even if it is not an adequate index of fertility status. The total phosphorus content of the surface soils of the United States in their virgin condition is shown in Fig. 1.

The area most deficient in total phosphorus is the coastal plain of the South Atlantic and Gulf States. From this low level the phosphorus content increases, generally speaking, to the north and west. It is particularly high in the Bluegrass Region of Kentucky, the Central Basin of Tennessee, and in some of the Northwestern States. The alluvial soils of the Lower Mississippi Valley reflect the relatively high phosphorus content of the soils of the Upper Mississippi and Missouri basins from which they are derived. In general, there is about a tenfold range in the phosphorus content of soils. Extreme variations, of course, are much greater. It may be inferred that the areas quite low in total phosphorus will need phosphorus fertilizers. Areas medium to high in total phosphorus may or may not require phosphorus fertilization for efficient crop production.

Figure 1 is based, in large part, on data on the chemical composition

of soils obtained in connection with the National Soil Survey (Marbut, 1935). The same body of data gives information on the distribution of phosphorus in the soil profile. That and other data relating to the phosphorus content of the subsoil have been reviewed by Winters and Simonson (1951). For many soils of the United States, the percentage of total phosphorus in the surface and subsurface layers does not differ greatly. Changes with depth are usually slight and may be in either direction, although in soils of the humid region there is a tendency for

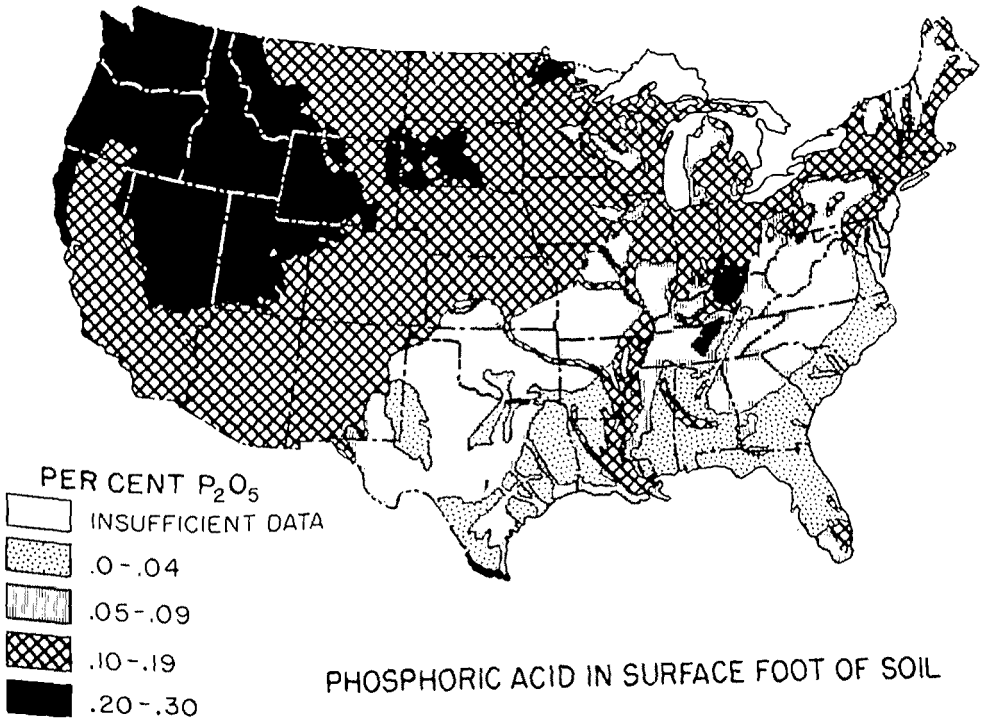


FIG. 1. Phosphoric acid in surface foot of soils in the United States.

a minimum somewhere between the A_1 and C horizons. Soils which have undergone podsolization exhibit a distinctly lowered phosphorus percentage in the leached layer and an accumulation of phosphorus in the B horizon. On the other hand, soils formed under limited rainfall are relatively uniform in phosphorus content throughout the profile.

Investigations also indicate a concentration of phosphorus in the soil colloid and, frequently, greater differences in the phosphorus content of the colloid than in that of the soil from the different horizons. This is illustrated by the data for Frederick silt loam (Alexander *et al.*, 1939) shown in Table I.

TABLE I

DISTRIBUTION OF PHOSPHORUS IN THE PROFILE OF FREDERICK SILT LOAM[a]

Horizon	Depth, inches	Per cent P_2O_5	
		Soil	Colloid
A_1	0–2	0.07	0.24
A_2	2–11	0.03	0.21
B_1	11–16	0.04	0.10
B_2	16–36	0.03	0.05
C	36–56	0.04	0.04
Parent rock		0.04	. . .

[a] Data of Alexander *et al.* (1939).

The total phosphorus content of soils is greatly influenced by the phosphorus content of the parent material. This seems to be the explanation for the major differences shown in Fig. 1. The high phosphorus soils of the Bluegrass Region and the Central Basin are derived from phosphatic limestone. In the same general region, soils from non-phosphatic limestone are relatively low in total phosphorus. The low-phosphorus soils of the Atlantic and Gulf Coastal Plains are derived, for the most part, from parent materials quite low in total phosphorus.

A study of Fig. 1 suggests the hypothesis that climate or a combination of climate, vegetation, and time materially influences the phosphorus content of soils. The general changes in content from south to north and from east to west may be partially explained by such a hypothesis.

Climate, vegetation, and time undoubtedly have a greater influence on the forms of phosphorus in soil and its availability to crops than on total phosphorus content. The Iowa and Nebraska Agricultural Experiment Stations have made important contributions in this field. Iowa investigators (Pearson and Simonson, 1940; Pearson *et al.*, 1940; Stelly and Pierre, 1943) have studied the amount and forms of phosphorus in the profile of about 20 soils representing the major soil associations of the state. Table II was compiled from their data. The trends are clearly evident. The organic phosphorus is highest in the surface soil and decreases steadily with increasing depth. Dilute acid-soluble phosphorus, like total phosphorus, is at a minimum concentration at 6 to 13 inches. The total phosphorus contents of the surface soil and the deep subsoil are essentially the same, but the dilute acid-soluble phosphorus content of the C horizons is much higher than that of the top soil. The same trends are apparent in all three of the Great Soil Groups studied—Prairie soils, Gray-Brown Podzolic soils, and Planosols. Lohse and

TABLE II

VERTICAL DISTRIBUTION OF ORGANIC, DILUTE ACID-SOLUBLE, AND TOTAL PHOSPHORUS

Horizon	Depth, inches	Phosphorus: Organic,[a] p.p.m.	Phosphorus: Dilute acid-soluble,[b] p.p.m.	Phosphorus: Total,[b] p.p.m.
Marshall silt loam				
Prairie				
A_1	0–6	264	17.4	698
	6–9	145	7.8	634
A_{11} and A_3	12–15	95	25.3	618
	18–21	61	73.0	633
C_1	24–27	28	107.0	759
	39–42	19	.....	...
C	54–57	. .	217.0	. .
	57–60	16	.....	855
Fayette silt loam				
Gray-Brown Podzolic				
A_1	0–1½	352	74	860
A_2	1½–4	230	42	639
A_{21}	4–7	167	23	552
B_1	10–13	67	12	396
B_2	16–19	45	26	507
B_{21}	28–31	26	38	579
B_3	40–43	24	92	718
C	49–54	22	118	732

[a] Data of Pearson and Simonson (1939).
[b] Data of Pearson *et al.* (1940).

Ruhnke (1933), in a study of Brown Forest soils in Canada, also found dilute acid-soluble phosphorus to be higher in the lower parts of the profile than in the top soil.

It would appear from the foregoing studies that, during the processes of soil formation, the inorganic phosphorus was changed from readily soluble calcium and magnesium phosphates to less soluble iron and aluminum phosphates, and, by the action of plants, to organic phosphates. Under conditions of higher rainfall and temperature, the phosphorus would probably have become even less soluble.

Allaway and Rhoades (1951) made a similar study with Chestnut and Chernozem soils developed from loess in southern Nebraska. The results are similar to those secured in Iowa. There is, however, one difference. In both of the two Chestnut soils and in two out of five of the Chernozems the maximum concentration of organic phosphorus is

found not at the surface but slightly below. In all of these soils except the most highly developed Chernozems, large amounts of organic phosphorus (more than 100 p.p.m.) are found at depths of 18 inches or greater.

Godfrey (1951) studied the distribution of phosphorus in five loess-derived soils taken along a traverse in southwestern Iowa and northern Missouri. All soil-forming factors were believed to be essentially constant except time, which increased in a southeasterly direction along the traverse. Table III gives the contents of total and organic phosphorus in the 0- to 24-inch section of the profile.

TABLE III

PHOSPHORUS IN SOILS OF DIFFERENT DEGREES OF WEATHERING[a]

Soil (*Degree of weathering increases from Minden to Putnam*)	*0–24 inches*	
	Total P, pounds/acre	*Organic P, pounds/acre*
Minden silt loam	4307	2064
Winterset silty clay loam	3910	1866
Haig silt loam	2841	1444
Edina silt loam	2830	1150
Putnam silt loam	2480	963

[a] Data of Godfrey (1951).

The data show a decrease in both total and organic phosphorus in the 0- to 24-inch section as the degree of weathering increases. Differences in the 24- to 48-inch section were small. The ratio of total phosphorus in the top section to that in the lower section declines from 0.89 in the Minden to 0.54 in the Putnam.

The amounts of organic phosphorus found in these profiles were of the same order of magnitude as found by the earlier workers. In the case of the two Planosol soils, this work does point out one new characteristic and that is an A_2 organic phosphorus content distinctly lower than is found in the layers immediately above and below.

III. Influence of Management on Phosphorus

Soil management practices may either lower or improve the phosphorus fertility of soils. The change may be produced by (1) removal of phosphorus, (2) additions of phosphorus, or (3) change in the forms of soil phosphorus. The major practices influencing phosphorus fertility will be considered with respect to both the kind and magnitude of the changes they produce.

1. Cropping

Cropping is a universal practice influencing the phosphorus fertility of soils. In some areas and on some fields of many farms it is the major practice. In other regions and fields it is less important than other practices, especially the application of manures and phosphatic fertilizers.

Growing and harvesting crops result in the annual removal of about 15 to 80 pounds of P_2O_5 per acre. As compared to crop removal of nitrogen and potash the removal of phosphorus is low. Even though the amounts removed are substantial, it does not follow that it is economic to replace these amounts of phosphorus or that on many soils the replacement of the amounts removed will be adequate for good production.

Loss of phosphorus due solely to cropping is usually rather small, especially when measured in terms of total soil phosphorus (Blair and Prince, 1936; Peevy *et al.*, 1940; Puhr and Olson, 1937). Cropping, however, not only removes phosphorus from the soil but alters the proportion of the various forms of inorganic and organic phosphates remaining in the soil. The crop removes so-called available phosphorus. This has been shown by comparing the amount of phosphorus removed by intensive cropping in a greenhouse experiment with the reduction in *A* value due to cropping (Rubins, 1952). The data are summarized in Table IV.

TABLE IV

PHOSPHORUS REMOVAL BY CROPS AND THE CHANGE IN *A* VALUE OF SOILS[a]

Soil type	*Phosphorus removed by crops, mg./pot*	*Reduction in A value by cropping, mg./pot*
Sassafras	76	98
Moyock	128	208
Caribou	219	165
Caribou	230	218
Caribou	90	92
Collington	122	141

[a] Data of Rubins (1953).

Kubota *et al.* (1948) have shown that cropping for 30 years materially reduced the readily soluble phosphorus in an irrigated Chestnut soil. The reduction in the surface foot varied from 66 to 78 per cent, depending on the rotation. Changes in readily soluble phosphorus at depths of 12 to 24 inches and 48 to 60 inches were larger than would be

expected. It may be, therefore, that the long storage of the virgin sample resulted in some changes that tended to magnify the differences.

Under limited rainfall, as in the Great Plains, cropping is almost the only management practice influencing fertility. Preliminary data (Haas, 1952) on soils from 13 dry-land field stations indicate that 35–45 years of cropping have not seriously impaired the phosphorus fertility of the soil. Total phosphorus was reduced less than 10 per cent. On the other hand, available phosphorus was slightly increased. The increase may have been due to the conversion of a considerable portion of the organic phosphorus to inorganic forms which had a high availability in these almost neutral soils.

The importance of phosphorus removal by cropping increases as agricultural production is increased. It is estimated, for example, that phosphorus removal by harvested crops increased from 1,372,000 tons of P_2O_5 in 1920 to 1,815,000 tons in 1947. Further increases in production will certainly result in the annual removal of more than 2,000,000 tons of P_2O_5.

2. Liming

Liming of acid soils usually increases the yields of most crops and is particularly effective in rotations which include legumes. (For a more complete discussion of the influence of liming on the availability of phosphorus, see Chapter IX.) The increase may be due to a change in a number of factors, including the availability of native and applied phosphates. It is extremely difficult to indicate quantitatively the several factors causing yield differences that result from liming. We should recognize that liming might reduce the availability of some nutrient but that the net effect would still be highly beneficial.

Salter and Barnes (1935) summarized a large volume of data on the influence of soil reaction on the availabilty of soil and fertilizer phosphorus. An analysis of long-term trends in yields and response to superphosphate in the Ohio five-year rotation experiment led to the conclusion that liming increases the availability of soil phosphorus. The influence of liming on soil phosphorus was also indicated in a legume-reaction experiment in which several grain crops were grown in a three-year rotation with different legume and hay crops on plots whose reaction varied from pH 4.7 to 7.5. The data are summarized in Table V (Ohio Agricultural Experiment Station, 1951).

When no phosphate was applied the highest average yields of both grain and hay crops were at pH 7.5, but when phosphate was used on corn and wheat in the rotation, the highest yields were at pH 6.8. The maximum response of grains to phosphate was at pH 5.7, of hay crops

at pH 6.8. Both grain and hay crops gave relatively little response to superphosphate when the soil was limed to pH 7.5. Almost maximum yields were secured without phosphorus. These data may be explained by assuming that liming increased the availability of soil phosphorus or that heavy liming reduced the efficiency of superphosphate. The relatively good yields make the first assumption very plausible.

TABLE V

CROP YIELDS AND RESPONSE TO SUPERPHOSPHATE[a] AT DIFFERENT SOIL REACTIONS[b]

Crops	*Treatment*	*Soil reaction, pH*				
		4.7	*5.0*	*5.7*	*6.8*	*7.5*
4 grain crops, bushels per acre	Phosphorus	20.9	28.8	36.7	40.1	38.6
	No phosphorus	14.8	19.2	23.3	30.6	34.7
	Increase	6.1	9.6	13.4	9.5	3.9
7 hay crops, pounds per acre	Phosphorus	587	936	2213	3743	3729
	No phosphorus	664	917	1603	2790	3524
	Increase	−77	29	610	953	205

[a] 500 lb. in a 3-year rotation.
[b] Data of Ohio Agricultural Experiment Station (1951).

The data of Table V clearly indicate that a good liming program to bring soils to reactions of 5.7 to 6.8 is essential for using superphosphate at maximum efficiency.

The influence of liming on the availability of phosphate fertilizers depends on the soil, the kind of phosphate used, and the crop being grown. As indicated in Table V, however, liming to pH 6.0 to 6.5 usually increases the efficiency of superphosphate and other water-soluble phosphate fertilizers. Other data show that liming tends to reduce the utilization of bonemeal, rock phosphate, and other phosphates of low solubility.

3. Farm Manure

Farm manure contains from 5 to 10 pounds of P_2O_5 per ton, with 7 pounds as a good average. Manure is usually applied at rates of 5 to 20 tons per acre, thus giving P_2O_5 applications of 35 to 140 pounds. Such a practice will obviously influence the phosphorus fertility of the soil.

New York investigators (McAuliffe and Peech, 1949; McAuliffe *et al.*, 1949) have shown that 50 to 85 per cent of the phosphorus in sheep and cow manure and in legume-grass forage is in inorganic forms. Using radioactive phosphorus techniques they showed that phosphorus in manure is just as available to ryegrass as phosphorus in

superphosphate. On this basis the phosphorus in farm manure applied to harvested crops in 1947 was equivalent to 4,000,000 tons of 20 per cent superphosphate.

Larson *et al.* (1952) have recently determined the influence of manure on the available phosphorus in soils as indicated by solubility and *A* values from field experiments. The determinations were on plots of long-time irrigated rotation experiments with Tripp fine sandy loam at Scottsbluff, Nebraska, and Pryor silty clay loam at Huntley, Montana. Both experiments were started in 1912. The data of Table VI are

TABLE VI

AVAILABLE PHOSPHORUS IN MANURED AND UNMANURED PLOTS OF ROTATION EXPERIMENTS[a]

Location	*Treatment*	*Available P_2O_5, pounds/acre*	
		H_2O-soluble	*A value*
Scottsbluff	Manure	44	320
	No manure	6	63
	Increase	38	257
Huntley	Manure	18	975
	No manure	6	468
	Increase	12	507

[a] Data of Larson *et al.* (1952).

from a three-year rotation of oats, sugar beets, and potatoes. The manured plots received 12 tons of manure every third year. It is estimated that a total of about 1000 pounds of P_2O_5 has been applied on the manured plots. The data indicate the great improvement in phosphorus fertility resulting from the use of manure. They confirm the early results that Kubota *et al.* (1948) obtained in studies of the Scottsbluff rotations.

The foregoing investigations indicate that manure increases inorganic phosphorus in the soil, but they do not afford much evidence on the effect of manure on organic phosphorus. Dean's (1938) study of the forms of phosphorus in soils of the Rothamsted and Woburn experiments gave good evidence on this point. The data show that manure increased both inorganic and organic phosphorus. About two-thirds of the total increase was in the inorganic form. The increase in organic phosphorus on the manured plots was only slightly larger than on the "minerals plus sulfate of ammonia" plots. Apparently when both phosphorus and nitrogen were adequate to produce high yields, there was an accumulation of organic phosphorus.

Associated with the manure problem is the movement of plant nutrients in commercial feeds. Mehring (1952), for example, found that in 1948 New England imported 35,500 tons of P_2O_5 in feeds as compared to 54,000 tons of P_2O_5 in fertilizers. Locally produced feeds contained an additional 31,700 tons of P_2O_5. Much the same situation prevails in some of the Middle Atlantic States. It is quite obvious from such data that imports of feeds combined with the effective conservation and use of farm manures can make an important contribution to the improvement of phosphorus fertility of a farm or state.

Large quantities of phosphorus are returned to the soil in straw and other crop residues. Like manure, a substantial proportion of the phosphorus is in the inorganic form and is as available to plants as the phosphorus in superphosphate. The phosphorus in farm manures, crop residues, composts, and green manures comes from the soil or the fertilizer used in producing the crop. The conservation and efficient use of manures and crop residues minimize the loss of phosphorus from the cycle. Their use may alter the form of phosphorus in the soil but would not increase the quantity.

4. Fertilizers

The liberal application of phosphate fertilizers is the most extensively used procedure for improving the phosphorus fertility of soils. The long-continued effects of phosphorus fertilization result from the fact that loss by leaching is negligible and the phosphorus retained in the soil is in forms that are somewhat available to crops, even several years after the fertilizer is applied. This, therefore, makes it possible to improve phosphorus fertility to a far greater degree than it is possible to increase the content of organic matter or the nitrogen fertility of soils.

The same soil and fertilizer reactions that make such improvement possible also reduce the efficiency of phosphorus fertilization. Numerous investigations, including those with radioactive phosphorus, show that the crop fertilized seldom contains more than 5 to 15 per cent of the phosphorus applied in the fertilizer. Since the efficiency is low, it usually requires relatively large applications of phosphates to produce maximum yields. Such applications are generally profitable and, therefore, extensively adopted. It is common practice for many farmers to apply two to ten times as much phosphorus in fertilizer as is removed by the crop. Obviously, when repeated over a period of years, this results in the accumulation of available phosphorus in the soil, thereby altering phosphorus fertilizer requirements and returns from its use.

The accumulation of phosphorus has been studied by several investigators (Bryan, 1933; Hawkins, 1946; Hawkins *et al.*, 1947; Peech, 1939,

1946). Representative data are given in Table VII to illustrate the magnitude of the changes that have been observed. It is evident that on soils devoted to the production of heavily fertilized crops, it is not unusual to find the level of available phosphorus 10 to 20 times higher than in comparable virgin soils.

TABLE VII

AVAILABLE PHOSPHORUS IN VIRGIN AND CULTIVATED SOILS

State	*Soil series*	*Major crop*	*Available phosphorus as P_2O_5 in*	
			Virgin soil, pounds/acre	*Cultivated soil, pounds/acre*
Alabama[a]	Norfolk-Ruston	Potato	12	300
Maine[a]	Caribou	Potato	34	219
Virginia[a]	Sassafras	Potato	45	808
Florida[b]	Norfolk	Citrus	63	543
New York[a]	Sassafras	Potato	15	778

[a] Data of Peech (1945).
[b] Data of Peech (1939).

The availability of the accumulated phosphorus has been shown to be rather high (Bryan, 1933; Hawkins *et al.*, 1947; Volk, 1945). The last study reports a rate-of-phosphorus-fertilizer experiment on plots which had received 0, 30, 60, 90, and 120 pounds of P_2O_5 annually during an initial 5-year period. During the second period (4 years), 30 pounds of P_2O_5 per acre produced increases of 463, 276, 91, 84, and 67 pounds of seed cotton per acre, respectively. When accumulations are large, the response to phosphorus fertilizers becomes small, just as on soils of high native-phosphorus fertility. It is seldom advisable, however, to discontinue completely the use of phosphorus, but the amount may be substantially reduced without an adverse effect on yields. The availability of the accumulated phosphorus is influenced by soil management and cropping practices. Liming, rotations, including legumes, the effective use of crop residues and farm manures, and the control of erosion will all contribute to maintaining the accumulated phosphorus in a form available to crops.

5. *Erosion*

The change in phosphorus fertility due to erosion varies widely with soil types and management. The phosphorus fertility status of the B horizon of soils in the humid region is usually lower than that of the surface soil. Much of this difference may be due to the differences in

forms of phosphorus rather than in total phosphorus. Such differences are increased when the fertility of the surface soil is improved through liming, manuring, and fertilization. As previously indicated, however, the phosphorus status of the subsoil and lower horizons of some soil types is as high or higher than that of the surface soil. On such soils erosion would not reduce, and might well improve, the phosphorus fertility of the soil, even though it might be quite harmful in other respects.

Erosion by either wind or water is often a selective process, the finer soil particles being removed in greater proportion than the coarser fraction (Stallings, 1951). The finer fractions are usually higher in phosphorus and other nutrient elements; thus the loss of available phosphorus may be several times greater than the loss of soil. Such losses may become quite high when the level of available phosphorus in the surface soil has been increased by fertilization. Scarseth and Chandler (1938) estimated that, in a 26-year experiment, 60 per cent of the phosphorus applied as superphosphate on a Norfolk sandy loam with a slope of 0.8 per cent had been carried away in a clay fraction lost by erosion. The estimated loss of rock phosphate in the same experiment was 82 per cent. Volk (1945), in somewhat similar investigations, estimated a loss of 25 per cent of the applied plus soil phosphorus in a 14-year experiment on Hartsell fine sandy loam in continuous cotton. In both of these experiments erosion was slight. The loss was chiefly due to the loss of soil colloids brought into suspension by the impact of rain on the surface of the soil. In both experiments the loss of phosphorus by erosion was about double the loss by crop removal. It is evident from such studies that estimates of changes in phosphorus fertility based primarily on additions of phosphorus and crop removal may lead to erroneous conclusions.

Water run-off even where there is little or no erosion may result in substantial losses of recently applied soluble phosphates. Rogers (1943) has shown that 9 to 20 per cent of the phosphorus applied as a top dressing of triple superphosphate on pastures may be lost in the surface run-off from a rain of high intensity immediately following the application of the fertilizer. There was negligible loss from water-insoluble phosphorus fertilizers or from triple superphosphate after the first heavy rain.

IV. Phosphorus Fertility Trends

Trends in phosphorus fertility may be estimated by a consideration of the relative impact of the several management practices that have been discussed. Estimates of trends may be made for an individual field, a farm, county, or state. The larger the unit, the greater the variations

within the unit. Nevertheless, for some purposes it is desirable to consider large units—states, regions, and the nation. It is also desirable to express trends quantitatively as far as possible. Reasonably satisfactory quantitative estimates can be made for phosphorus removal by crops and additions to the soils. These will be used as one indication of fertility trends. Other factors involving trends will be discussed in more general terms. Finally, the evidence available from the analysis of soils will be considered.

The data to be presented are necessarily for large units and are often expressed in average rates per acre. This obscures the large and very important variations within the unit for which averages are given. In guiding fertilizer practices on a farm it is essential to know fertility levels by fields or parts of fields. For estimating state or national trends in fertility, averages and other data for large units are useful, but the range of values going to make up the average for the unit should never be forgotten.

Most of our data on trends in phosphorus fertility relate primarily to croplands as contrasted to pastures and other noncroplands on the farm. Data on phosphorus removals and additions to croplands for the period 1910–1955 are given in Table VIII. These data indicate that,

TABLE VIII

ESTIMATED REMOVAL OF P_2O_5 BY HARVESTED CROPS AND ADDITIONS TO SOILS AS FERTILIZERS AND FARM MANURES IN THE UNITED STATES, 1910–1955

THOUSANDS OF TONS

Year	*Removal by harvested crops*[a]	*Applied to crops in*			*Balance, column 5 − column 2*
		Fertilizers[b]	*Manures*[c]	*Total*	
1910	1103	490	631	1121	18
1920	1372	640	727	1367	−5
1930	1291	771	655	1426	135
1940	1439	894	615	1509	70
1950	1830	2434	805	3239	1409
1955	1897	3785	876	4661	2764

[a] Estimated on basis of the production and average phosphorus content of major crops.

[b] P_2O_5 in all fertilizers, including 300,000 tons of P_2O_5 as phosphate rock in 1955.

[c] Estimated from livestock population and manure composition and utilization reported by Mehring and Parks, 1949.

for 30 or 40 years, additions of phosphorus in the United States as fertilizers and manures have approximately balanced removal of phosphorus by harvested crops. If losses by erosion were included, the balance would certainly be strongly negative. Only since World War II has the use of phosphorus fertilizers risen to a level that may provide a substantial

positive balance. If the 1955 goals (Minor, 1952; United States Department of Agriculture, 1952) of phosphorus fertilizer production and use are attained, additions will be 245 per cent of estimated removal by harvested crops.

It would appear from these data that currently the phosphorus fertility of cropland is not declining. If the 1955 goals for fertilizer consumption are attained and maintained for a period of years, the fertility status of cropped soils should be expected to increase. These data, however, do not reflect the possible influence of several important factors; neither do they indicate the differences in trends in different regions or states.

The favorable influence of liming on the availability of native and applied phosphorus was indicated in Section III.2. It is appropriate, therefore, to consider trends in lime consumption and its effect on phosphorus fertility. Lime consumption apparently ranged from 1,000,000 tons to 3,000,000 tons annually in the period 1910–1930. By 1940 it was 13,434,000 tons, and in 1950, 26,536,000 tons. This great and sustained use of lime has doubtless contributed to the improvement of the phosphorus fertility of our soils. If consumption should reach 40,000,000 tons of liming materials by 1955, the improvement would be even more substantial.

The estimates of manure use indicated in Table VIII are based primarily on livestock population and an estimate of percentage utilization. They do not reflect possible changes in the efficiency of storage and utilization of manures. It seems probable that with increased mechanization and improvements in livestock housing and management, utilization of manures is also being improved. Certainly, this seems to be the case on many dairy farms. There is obviously a need for improving the utilization of this important source of plant nutrients and organic matter. It may well be, therefore, that improvements in manure utilization will contribute substantially to improvements in fertility.

Quantitative estimates of the influence of erosion on phosphorus fertility have not been presented. The losses have been large; there is no doubt about that. During the last 15 to 20 years such losses have certainly been substantially reduced. Concerted efforts for better soil and water conservation and management are being reflected in improved phosphorus fertility, as well as in improved soil fertility and crop production generally.

A consideration of trends in the major soil management practices, therefore, indicates that the trend of phosphorus fertility in U. S. soils devoted to crop production is probably upward, marked by a steady and substantial improvement, especially if 1955 goals for phosphorus ferti-

lizer production and use are attained. This improvement, however, may not be taking place in all sections of the United States. Some areas may be steadily declining in fertility, others improving rapidly. Regional and state differences are indicated in Fig. 2, which shows the balance between additions and removal of P_2O_5 on cropland for 1947. The Eastern and Southern States show large positive balances. The balance in the East North Central States is positive but smaller. In the

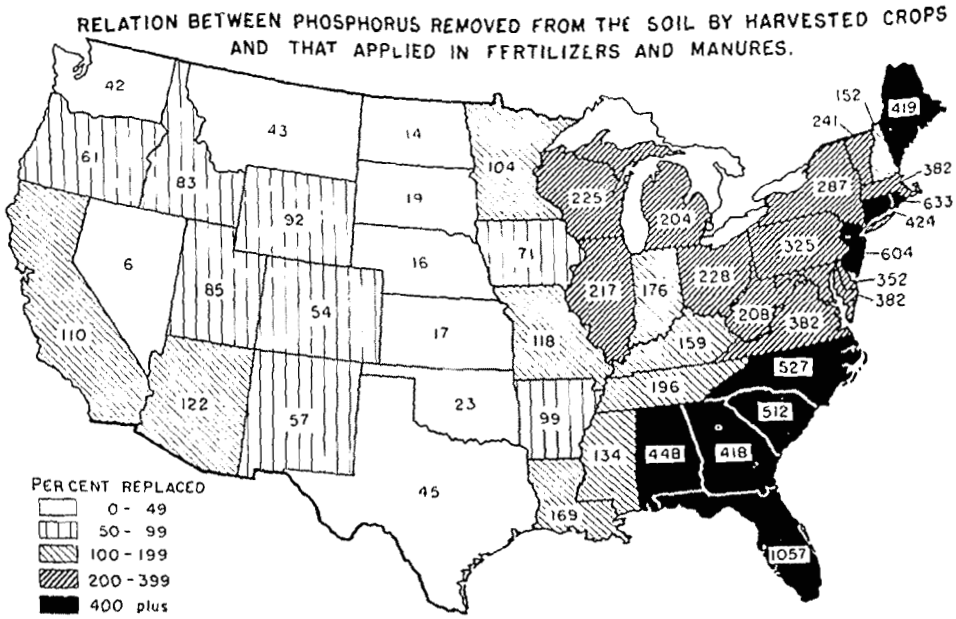


FIG. 2. Relation between phosphorus removed from the soil by harvested crops and that applied in fertilizers and manures.

Great Plains, from Texas to North Dakota, additions are only about 20 per cent of phosphorus removals by cropping.

Regional trends are also indicated by the data of Table IX. It is evident that for at least 30 years, New England and the Middle Atlantic and South Atlantic Regions have had a very favorable phosphorus balance on cropland if losses by erosion are not included. The East North Central and East South Central Regions had a small positive balance in 1920. It increased in 1947 and will be sufficiently large if 1955 goals are made to insure marked improvement in phosphorus fertility over a period of several years. Phosphorus additions in three regions—West North Central, West South Central, and Pacific Coast—were substantially lower than phosphorus removal in harvested crops in 1920 and 1947. The 1955 goals, however, provide for a small positive

balance. There are, of course, good reasons for these regional differences. They include differences in the phosphorus fertility of soils and climatic differences, of which precipitation available for crop production is one of the more important.

TABLE IX

ESTIMATED PER CENT OF PHOSPHORUS REMOVED IN HARVESTED CROPS THAT IS REPLACED BY FERTILIZER AND MANURE[a]

Region	*1930*	*1947*	*1955*
New England	816.6	364.7	408.2
Middle Atlantic	281.2	350.2	470.4
South Atlantic	682.8	544.0	676.7
East North Central	142.0	216.0	366.4
East South Central	126.8	266.3	403.3
West North Central	41.1	51.1	105.0
West South Central	19.0	65.4	173.8
Mountain	128.3	74.2	108.4
Pacific	54.9	90.9	144.8
Continental U. S.	124.4	152.7	245.6

[a] See Table VIII for basis of estimates.

In the United States the use of fertilizer on noncropland is small. It was very small during 1920–1940. As recently as 1947 it was estimated that only 10 per cent of the phosphorus applied as fertilizers was used on pasture and noncrop agricultural land. This is an exceedingly small quantity for the 47,449,000 acres of cropland pasture and 481,016,000 acres of pasture other than cropland and woodland (United States Bureau of Census, 1947). Much of this land is in the West where water is the limiting factor, and, therefore, returns from fertilizers might be small and uncertain. There are, however, 30,126,000 acres of cropland pasture and 72,221,000 acres of other nonwoodland pasture in the 31 states of the humid region. This compares with 183,864,000 acres of harvested cropland in the same states.

Phosphorus removal by grazing of noncropland has probably been small; often erosion is more important. For the most part, the phosphorus status of noncropland is probably somewhat lower than that of virgin soil. There are tens of millions of acres of pasture in the humid regions of the United States on which production is low and limited by reason of lack of available phosphorus. No substantial improvement in production on such lands can be secured without the additions of phosphorus. Usually this will require an initial application of 100 to 300 pounds of P_2O_5 per acre and smaller additions for maintenance. Generally, additions of lime and potash are also required.

Probably the most reliable method of following fertility trends is the analysis of representative soils at 5- or 10-year intervals. Such data are limited. There are, however, considerable data on virgin and cultivated soils. As previously indicated, those data show large accumulations of available phosphorus where there have been substantial additions of manure and phosphorus fertilizers but only small to moderate changes due to cropping.

State soil-testing laboratories provide useful data on trends in soil fertility, especially when the data are studied in relation to other information on soils, crops, and fertilizer practices. Such data for North Carolina (Welch and Nelson, 1951) are given in Table X. The crops

TABLE X

LEVEL OF PHOSPHORUS USE, SOIL TESTS, AND RETURNS FROM INCREASED PHOSPHORUS FERTILIZATION BY CROPS IN NORTH CAROLINA

		Soils testing[b]			
Crop	P_2O_5 *used, pounds/acre*[a]	*Very low or low in phosphorus, per cent*	*Very high or high in phosphorus, per cent*	*Increase from additional 40 pounds,*[a] *per cent*	*Acreage, 1000 acres*[a]
Potatoes	120	13	84	0	61
Tobacco	115	11	82	0	619
Cotton	55	20	81	4	860
Corn	27	40	43	7	2159
Pasture	19	76	16	48	1577
Hay	1	66	24	82	1205

[a] Data of National Soil and Fertilizer Research Committee (1951).
[b] Data of Welch and Nelson (1951).

are listed in the order of the level of phosphorus fertilization. The level of available phosphorus in soil samples taken from fields to be planted to these crops correlates with the rate of fertilization. Only 12 per cent of the samples from potatoes and tobacco fields are very low or low in phosphorus. Eighty per cent of the samples tested high or very high. The estimated return from an additional 40 pounds of P_2O_5 per acre is zero. As a matter of fact, it is estimated that a 25 per cent reduction in the use of phosphorus would reduce the yield of potatoes only 2 per cent and the yield of tobacco less than 1 per cent (National Soil and Fertilizer Research Committee, 1951). Phosphorus fertilization of cotton and corn is substantially lower, as is the level of soil phosphorus in cotton and corn fields. The estimated return from additional phosphorus is larger but still relatively small. The soil samples from pasture and

hay fields show really low levels of available phosphorus. Two-thirds or more of the soil samples were very low or low in available phosphorus. Here additional phosphorus gives large returns.

The trend of phosphorus fertility in the 17 Western States depends largely on whether the land is irrigated. Unless they are fertilized or manured, irrigated soils decline in phosphorus fertility on cropping, especially when large crops of alfalfa are removed. The decline may be severe, as indicated by previously cited data from Nebraska and Montana experiments. On the other hand, nearly all the manure and phosphorus fertilizer used in the West is applied to irrigated land. Very little is used on nonirrigated land except in the limited humid areas of the Pacific Coast and in the eastern part of the Great Plains States. On irrigated soils, therefore, the trend in phosphorus fertility is more favorable than might be inferred from the data of Table IX or from Fig. 2. Unfortunately, there are not enough soil analysis data to evaluate adequately the changes.

The data on phosphorus removal and additions for dry-land soils indicate a probable decline in phosphorus fertility. Recent analytical data for virgin soil and variously cropped plots from 13 field stations do not indicate such a decline. As a matter of fact, there is apparently an increase of available phosphorus on cultivated but unmanured plots. If such data are confirmed by subsequent investigations, the trend in phosphorus fertility would be much more favorable than is indicated by the data of Fig. 2 and Table IX.

V. Phosphorus Requirements

The use of phosphorus fertilizers in the United States should be at a level that will assure the efficient production of the desired volume of crops and also steadily improve the level of available phosphorus in soils deficient in that nutrient. The rate of phosphorus fertilization required for good production will depend on the phosphorus status of the soil and the degree to which other factors, including nutrients and water, are limiting yields. Desirable levels may be estimated from farm practice, soil analysis, field experiments, and the experience of other countries.

Experience in the East and South indicates that when potatoes, tobacco, and other crops are fertilized with 75 pounds or more of P_2O_5 per acre, there is a large accumulation of available phosphorus in the soil and returns from continued phosphorus fertilization become small. A 1938 survey (Smalley *et al.*, 1939) indicated that the average rate of fertilization of cotton in North Carolina was 436 pounds of complete fertilizer, which probably contained 36 pounds of P_2O_5. The rate of

fertilization increased to 55 pounds of P_2O_5 per acre in 1950 (National Soil and Fertilizer Research Committee, 1951). These rates have resulted in a large accumulation of available phosphorus, as indicated by the data given in Table X.

The Illinois Agricultural Experiment Station (1949) used the data of county soil laboratories along with extensive field experiments as a basis for estimating phosphorus requirements. The summary for the states indicates that 16,162,00 acres of cropland out of a total of 25,-133,000 acres are deficient in available phosphorus. It is estimated that 158,800 tons of P_2O_5 in superphosphate or its equivalent are needed annually to correct this deficiency and improve fertility as well as crop production. This is equivalent to 13 pounds P_2O_5 per acre of cropland in Illinois or 20 pounds P_2O_5 per acre of cropland deficient in phosphorus.

The long-time fertilizer and rotation experiment of the Pennsylvania Agricultural Experiment Station (Noll *et al.*, 1931) received 24 pounds of available P_2O_5 per acre annually. Fifty-year average yields on the limed plots were: 50 bushels corn, 57 bushels oats, 29 bushels wheat, and 1.7 tons hay. In the Ohio five-year rotation experiment, superphosphate was applied at the rate of 15.5 pounds of P_2O_5 per acre annually. Yields on the limed plots were similar to those reported from Pennsylvania. Other Ohio data (Ohio Agricultural Experiment Station, 1951) indicate that in grain-hay rotations there is little or no return from applying more than twice as much phosphorus as is removed by the crop. At three locations high yields were obtained from annual applications of 26, 30, and 38 pounds of available P_2O_5 per acre. These data were obtained on soils that furnish 15 to 20 pounds of P_2O_5 per acre to unfertilized crops.

In many of the experiments of the Illinois Station (Bauer, 1945), 4 tons of rock phosphate per acre were applied prior to 1924, with no subsequent applications. This is an average of 60 pounds of total P_2O_5 per acre per year for a 40-year period. The plots so treated are still producing well, indicating a good level of available phosphorus. In 1924 the Illinois Station initiated experiments with superphosphate applied at an annual rate of 33 pounds of P_2O_5 per acre. On limed land the superphosphate produced somewhat larger yields than rock phosphate at the higher rates. Volk (1945) found that during an initial 5-year period, 30 pounds of available P_2O_5 per acre applied annually to cotton produced about 75 per cent of the maximum increases obtained from phosphorus and resulted in substantial improvement in available phosphorus in the soil, as evidenced by residual effects which persisted over a 9-year period, the duration of the experiment. It may be con-

cluded, therefore, that the evidence of field experiments indicates that in the humid region annual rates of about 30 pounds of P_2O_5 are adequate for above-average crop production and substantial soil improvement over a period of time.

This figure of 30 pounds of fertilizer P_2O_5 per acre is similar to the rate of phosphorus fertilization in several European countries in 1950–1951 (Organization for European Economic Co-operation, 1951). In Germany, for example, the average rate was 26 pounds of P_2O_5 per acre of agricultural lands (omitting rough grazing). The corresponding figures for France, Denmark, and the United Kingdom are 15, 23, and 32 pounds, respectively. The rate in The Netherlands was 48 pounds per acre, the highest of any nation in the world. Bruin *et al.* (1951) and Visser (1952) indicated that the levels of phosphorus fertility of Netherland soils have been increased to the point that the use of more phosphorus would not increase yields more than 1 or 2 per cent. European experience, therefore, indicates that the annual use of around 30 pounds of fertilizer P_2O_5 will give high yields and that the maximum economic rate may be 50 pounds, or somewhat less. In evaluating European data, it should be remembered that erosion losses are lower than in the United States and that manure preservation and use are better than in most regions of the United States.

The National Soil and Fertilizer Research Committee (1951) has summarized data on the response of crops to nitrogen, phosphorus, and potash fertilization in each state. The response indicated for each of the nutrient elements assumes that the other two elements are not limiting yields. This results in greater estimated returns from phosphorus than would be achieved in practice. The U. S. summary gives the weighted average change of crop values at different levels of phosphorus fertilization. The current average rate of 9 pounds per acre is based on an acreage of 561,000,000 acres. The returns from phosphorus fertilization are shown in Fig. 3, which also indicates current levels and 1955 goals of phosphorus fertilization. The data indicate a return of $4.28 per dollar invested in phosphorus fertilizer, 5 cents per pound of P_2O_5, at current levels of use. The 1950–1955 increment would give a return of $2.56 and a similar additional increment would give a return of $1.45 per dollar invested. It would appear, therefore, that the 1955 goals are near the maximum economical rate of phosphorus fertilization at current crop and fertilizer prices.

These data, however, are based on a uniform percentage increase in phosphorus fertilization of all crops currently fertilized. Obviously, the return would be substantially better if the additional phosphorus were used on the more phosphorus-deficient soils and on crops most re-

sponsive to phosphorus fertilization. Such selective use of the additional phosphorus fertilizer would, in large measure, result in most of it being used on relatively low-per-acre-value crops. This would tend to hold dollar returns low even though the physical return might be high.

The levels of phosphorus use in 1950 and goals for 1955 are given by regions in Table XI. The average rates are for total cropland, which

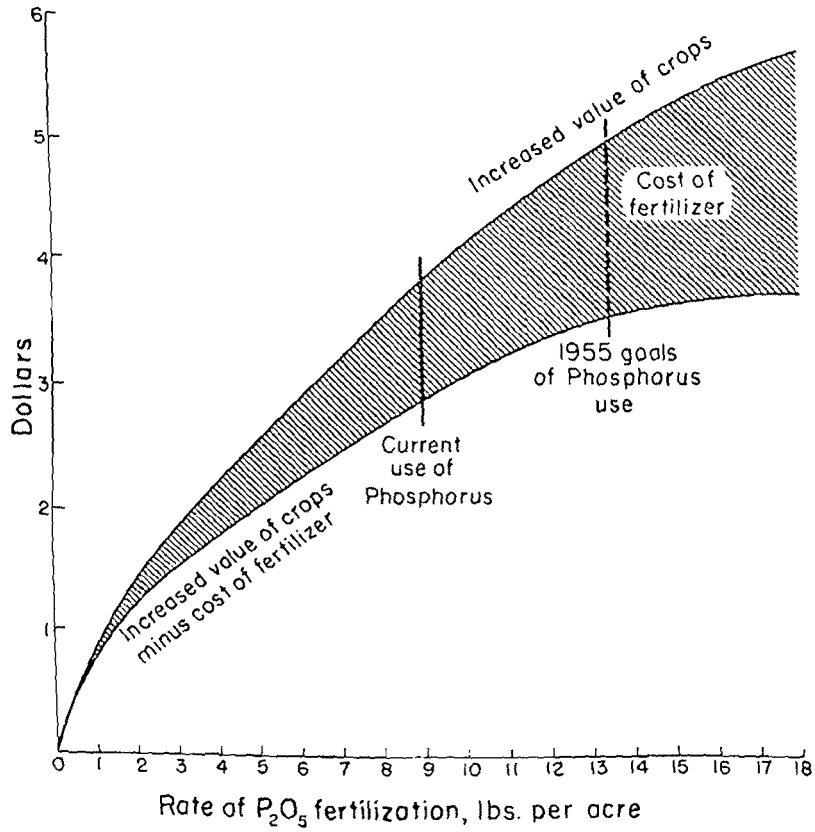


FIG. 3. Average value of phosphorus response for all crops in the United States.

includes 47,449,000 acres of cropland pastures and 50,379,000 acres from which crops were not harvested. No allowance, however, is made for phosphorus use on the 481,000,000 acres of "pasture other than cropland and woodland." The data show that the three regions adjacent to the Atlantic and Gulf Coasts were using 25 to 30 pounds of P_2O_5 per acre from fertilizer and total applications of 30 to 43 pounds in 1950. The estimated levels of use in 1955 are 29 to 44 pounds of fertilizer P_2O_5 and 39 to 59 pounds of total P_2O_5. In these three regions the projected level of fertilizer use approaches that of The Netherlands.

TABLE XI

ESTIMATED RATES OF PHOSPHORUS FERTILIZATION ON CROPLAND[a]

Region	P_2O_5 per acre from Fertilizers, pounds 1950	Fertilizers, pounds 1955[b]	Fertilizers and manure, pounds 1950	Fertilizers and manure, pounds 1955[b]
New England	25.0	29.0	37.9	43.2
Middle Atlantic	29.8	44.0	43.4	59.0
South Atlantic	29.4	38.8	30.0	39.5
East North Central	16.8	30.1	25.7	39.9
East South Central	19.2	23.6	19.9	24.4
West North Central	3.5	6.2	5.9	8.8
West South Central	5.9	10.5	6.1	10.8
Mountain	2.8	5.4	7.1	10.2
Pacific	7.2	11.9	9.2	14.2
Continental U. S.	10.8	16.8	14.3	20.7

[a] U. S. Census, 1943: Cropland harvested 352,865,765 acres, crop failure 10,297,172 acres, cropland idle or fallow 40,082,105 acres, and cropland used only for pasture 47,449,184 acres.

[b] Based on estimated regional consumption of 1955 phosphorus fertilizer production goals.

The two East Central Regions used 17 and 19 pounds of fertilizer P_2O_5 in 1950, with manure making a total application of 20 to 26 pounds. Estimates for 1955 are for 24 and 30 pounds of fertilizer and 24 and 40 pounds of total P_2O_5 per acre. The relatively low values for the East South Central Region are due, in part, to the fact that the soils of three important agricultural areas, the Bluegrass Region of Kentucky, the Central Basin of Tennessee, West Tennessee and the Delta of the Mississippi, are relatively high in available phosphorus. In the four Western Regions the current level of fertilizer use is less than 10 pounds per acre, including manure, with an estimated 1955 application of 9 to 14 pounds per acre. All four of these regions included very large acreages of dry land, where the general need for phosphorus fertilizer has not been clearly established.

Experimental data on crop response to phosphates and the experience of the older fertilizer-consuming states and that of other countries indicate that the 1955 goals for phosphorus fertilizer consumption are adequate for our crop production goals and for improvement in the phosphorus fertility of our soils. Requirements would be increased substantially if the profitable use of phosphates were demonstrated on the dry-land soils of the West or if an extensive acreage of pasture were to be improved in a short time. The 3,785,000 tons of P_2O_5 in fertilizers, however, would be adequate for a considerable percentage increase in the proportion of phosphorus fertilizer used on grassland crops, espe-

cially on the 47,449,000 acres of cropland pasture. They would not be adequate for a rapid and extensive improvement in pasture production on the 481,000,000 acres of "pasture other than cropland and woodland," of which 72,000,000 acres are in the 31 states of the humid region. With those two qualifications, it would appear that the annual use of 3,785,000 tons of fertilizer P_2O_5 plus 876,000 tons of P_2O_5 in manure would be adequate for crop production and soil improvement for a considerable period. This assumes a very efficient distribution of use on soils and crops. Actually, such an efficient distribution will not be obtained. Some fertile soils and high-per-acre-value crops will receive more phosphorus than is required, thereby reducing the quantity available for use on other soils and crops. It may well be, therefore, that the requirement for fertilizer P_2O_5 in the United States may exceed the 1955 goal by 500,000 to 1,000,000 tons within the next 10 to 15 years.

References

Alexander, L. T., Byers, H. G., and Edgington, G. 1939. A chemical study of some soils derived from limestone. *U. S. Dept. Agr. Tech. Bull.* **678.**

Allaway, W. H., and Rhoades, H. F. 1951. Forms and distribution of phosphorus in the horizons of some Nebraska soils in relation to profile development. *Soil Sci.* **72**: 119–128.

Bauer, F. C., Lang, A. L., Badger, C. J., Miller, L. B., Farnham, C. H., Johnson, P. E., Marriott, L. F., and Nelson, M. H. 1945. Effects of soil treatment on soil productivity. A summary of long-time field experiments. *Illinois Agr. Expt. Sta. Bull.* **516.**

Blair, A. W., and Prince, A. L. 1936. Some effects of long-continued manure, fertilizer, and lime treatment on the composition of cropped soils. *New Jersey Agr. Expt. Sta. Bull.* **604.**

Bruin, P., Castenmiller, G. M., Mulder, E. G., Paauw, F. v.d., and 't Hart, M. L. 1951. Possibilities of improving the fertility of the soil in The Netherlands by more rational application of lime, inorganic and organic manures and by improvement of its texture. *United Nations Sci. Conf. Conservation Utilization Resources, Proc.* **1949**, 6: 217–220.

Bryan, O. C. 1933. The accumulation and availability of phosphorus in old citrus grove soils. *Soil Sci.* **36**: 245–259.

Dean, L. A. 1938. An attempted fractionation of the soil phosphorus. *J. Agr. Sci.* **28**, Pt. 2: 234–244.

Dean, L. A. 1952. The evaluation of phosphorus fertility of soils through the medium of radiophosphorus. *Trans. Intern. Soc. Soil Sci. Commissions II and IV Dublin* **1**: 48–52.

Fried, M., and Dean, L. A. 1952. A concept concerning the measurement of available soil nutrients. *Soil Sci.* **73**: 263–271.

Godfrey, C. L. 1951. Distribution and nature of phosphorus in a geochronosequence of loess-derived soils. Unpublished Ph.D. thesis, Iowa State College, Ames, Iowa.

Haas, H. J. 1952. Unpublished data.

Hawkins, A. 1946. Nutrient status of soils in commercial potato-producing areas of

the Atlantic and Gulf Coast: III. Plant responses to fertilization. *Soil. Sci. Soc. Amer. Proc.* **10**: 252–256.

HAWKINS, A., CHUCKA, J. A., and MACKENZIE, A. J. 1947. Fertility status of potato soils of Aroostook County, Maine, and relation to fertilizer and rotation practices. *Maine Agr. Expt. Sta. Bull.* **454**.

ILLINOIS AGRICULTURAL EXPERIMENT STATION. 1949. Total potash and phosphate in Illinois. 4 pp. (*mimeographed*).

KUBOTA, J., RHOADES, H. F., and HARRIS, L. 1948. Effects of different cropping and manurial practices on some chemical properties of an irrigated Chestnut soil. *Soil Sci. Soc. Amer. Proc.* **12**: 304–309.

LARSON, W. E., COSPER, H. R., and OLSEN, S. R. 1952. Unpublished data.

LOUISE, H. W., and RUHNKE, G. N. 1933. Studies on readily soluble phosphate in soils: II. The vertical distribution of readily soluble phosphate in some representative Ontario soils. *Soil Sci.* **35**: 459–468.

MCAULIFFE, C., and PEECH, M. 1949. Utilization by plants of phosphorus in farm manure: I. Labeling of phosphorus in sheep manure with P^{32}. *Soil Sci.* **68**: 179–184.

MCAULIFFE, C., PEECH, M., and BRADFIELD, R. 1949. Utilization by plants of phosphorus in farm manure: II. Availability to plants of organic and inorganic forms of phosphorus in sheep manure. *Soil Sci.* **68**: 185–195.

MARBUT, C. F. 1935. Soils of the United States. Atlas of American Agriculture, Pt. 3, U. S. Department of Agriculture, Washington.

MEHRING, A. L., and PARKS, R. Q. 1949. How nutrients removed from soil by harvested crops are replaced by fertilizers. *Agr. Chemicals* **4**(10): 36–40; (11): 33–37, 39, 77–78.

MEHRING, A. L., and PARKS, R. Q. 1950. Are we replacing soil nutrients removed with crops? *What's New in Crops & Soils* **2**(9): 10–13, 24.

MEHRING, A. L. 1952. Unpublished data.

MINOR, W. A. 1952. Our job in fertilizer utilization. *Plant Food J.* **6**(2): 12–13, 40–41.

NATIONAL SOIL AND FERTILIZER RESEARCH COMMITTEE. 1951. *Rept. 1:* Fertilizer use and crop yields in the Southern Region. *Rept. 2:* Fertilizer use and crop yields in the North Central Region. *Rept. 3:* Fertilizer use and crop yields in the Northeastern Region. *Rept. 4:* Fertilizer use and crop yields in the Western Region. *Rept. 5:* Fertilizer use and crop yields in the United States. [Processed.]

NELSON, W. L., and HAWKINS, A. 1947. Response of Irish potatoes to phosphorus and potassium on soils having different levels of these nutrients in Maine and North Carolina. *J. Am. Soc. Agron.* **39**: 1053–1067.

NOLL, C. F., GARDNER, F. D., and IRVIN, C. J. 1931. Fiftieth anniversary of the general fertilizer tests. *Pennsylvania Agr. Expt. Sta. Bull.* **264**.

OHIO AGRICULTURAL EXPERIMENT STATION. 1951. Handbook of Ohio Experiments in Agronomy. 204 pp. Wooster, Ohio.

ORGANISATION FOR EUROPEAN ECONOMIC CO-OPERATION. [1951.] Fertilisers in Agricultural Recovery Programmes. 56 pp. Le Moil & Pascaly, Paris.

PARKER, F. W. 1950. Phosphorus in soils and fertilizers. *Science* **111**: 215–220.

PEARSON, R. W., and SIMONSON, R. W. 1939. Organic phosphorus in seven Iowa soil profiles: Distribution and amounts as compared to organic carbon and nitrogen. *Soil Sci. Soc. Amer. Proc.* **4**: 162–167.

PEARSON, R. W., SPRY, R., and PIERRE, W. H. 1940. The vertical distribution of total and dilute acid-soluble phosphorus in twelve Iowa soil profiles. *J. Amer. Soc. Agron.* **32**: 683–696.

PEECH, M. 1939. Chemical studies on soils from Florida citrus groves. *Florida Agr. Expt. Sta. Bull.* **340.**

PEECH, M. 1946. Nutrient status of soils in commercial potato-producing areas of the Atlantic and Gulf Coast: Part II. Chemical data on the soils. *Soil Sci. Soc. Amer. Proc.* **10**: 245–251.

PEEVY, W. J., SMITH, F. B., and BROWN, P. E. 1940. Effects of rotational and manurial treatments for twenty years on the organic matter, nitrogen, and phosphorus contents of Clarion and Webster soils. *J. Am. Soc. Agron.* **32**: 739–753.

PRINCE, A. L., and BEAR, F. E. 1948. Phosphorus needs of New Jersey soils. *New Jersey Agr. Expt. Sta. Bull.* **744.**

PUHR, L. F., and OLSON, O. 1937. A preliminary study of the effect of cultivation on certain chemical and physical properties of some South Dakota soils. *South Dakota Agr. Expt. Sta. Bull.* **314.**

RHOADES, H. F. 1939. Effect of organic matter decomposition on the solubility and fixation of phosphorus in alkaline soils. *Nebraska Agr. Expt. Sta. Research Bull.* **113.**

ROGERS, H. T. 1942. Losses of surface-applied phosphate and limestone through runoff from pasture land. *Soil Sci. Soc. Amer. Proc.* **7**: 69–76.

RUBINS, E. J. 1953. Residual phosphorus of heavily fertilized acid soils. *Soil Sci.* **75**: 59–67.

SALTER, R. M., and BARNES, E. E. 1935. The efficiency of soil and fertilizer phosphorus as affected by soil reaction. *Ohio Agr. Expt. Sta. Bull.* **553.**

SCARSETH, G. D., and CHANDLER, W. V. 1938. Losses of phosphate from a light-textured soil in Alabama and its relation to some aspects of soil conservation. *J. Am. Soc. Agron.* **30**: 361–374.

SMALLEY, H. R., ENGLE, R. H., and WILLETT, H. 1939. American fertilizer practices (second survey). 128 pp. National Fertilizer Association, Washington, D. C.

SMITH, F. B., BROWN, P. E., and PEEVY, W. J. 1937. Effect of long-continued treatment on the organic matter, nitrogen, and phosphorus content of Clarion loam. I. Continuous corn. *Iowa State College J. Sci.* **11**: 379–395.

STALLINGS, J. H. 1951. Soil-fertility losses by erosion. *Better Crops with Plant Food* **35**(8): 21–26, 45–47.

STELLY, M., and PIERRE, W. H. 1942. Forms of inorganic phosphorus in the C horizons of some Iowa soils. *Soil Sci. Soc. Amer. Proc.* **7**: 139–147.

UNITED STATES BUREAU OF THE CENSUS. 1947. United States Census of Agriculture: 1945. Vol. 2. Washington.

UNITED STATES DEPARTMENT OF AGRICULTURE. 1952. Agriculture's capacity to produce. *Agr. Inform. Bull.* **88.**

VISSER, W. C. 1952. Agriculture. *Soil Sci.* **74**: 1–13.

VOLK, G. W. 1945. Response to residual phosphorus of cotton in continuous culture. *J. Am. Soc. Agron.* **37**: 330–340.

WELCH, C. D., and NELSON, W. L. 1951. Fertility status of North Carolina soils as shown by soil tests. North Carolina Department Agriculture, Raleigh.

WINTERS, E., and SIMONSON, R. W. 1951. The Subsoil. Advances in Agron. **3**, 1–92.

CHAPTER XIV

Factors Influencing Phosphate Usage in Great Britain

A. B. STEWART

I. Land Utilization and Fertilizer Consumption in Great Britain

1. Land Utilization

In any discussion of problems of soil fertility and crop production on a regional or area basis, existing land utilization is a primary background consideration. Table I shows in broad outline how the 93,000 square miles of land surface of Britain are at present utilized.

TABLE I

LAND UTILIZATION IN GREAT BRITAIN
(Land classes as percentages of total land areas)

	England and Wales	*Scotland*	*Northern Ireland*	*United Kingdom*
Area in acres	37,131,675	19,069,000	3,352,251	59,552,926
Rough grazings, including mountain and health	14.6	57.4	21.4	28.7
Total crops and grass	65.6	23.1	67.4	52.1
Permanent grass	28.1	6.2	31.1	21.3
Total arable, including:	37.5	16.9	36.3	30.8
Tillage	27.5	9.3	19.1	21.2
Rotation grass for hay	6.4	2.1	6.7	5.0
Rotation grass for grazing	3.6	5.5	10.5	4.6

The rough grazings referred to in the first category include all the mountain and heath lands described, euphemistically in many cases, as used or capable of being used as grazings. They include scree slopes on the mountains, several million acres of peat of widely varying depth, and for the rest, a varying depth of raw humus overlying a scanty layer of mineral soil. Depending on climate, soil, and drainage, this land carries an inferior vegetation of the common moorland species

—Scirpus, Eriophorum, Molinia, Calluna, Erica, Juncus, Nardus, etc., with the more nutritive agrostis, fescues, sweet vernal, and other grasses on the better mineral areas. It will be seen that this class of land is particularly extensive in Scotland, where the total under crops and grass is less than one quarter of the land area, as contrasted with about two-thirds in the remainder of the British Isles and about one half in the British Isles as a whole. Further it will be noted that the area classed as agricultural land amounts to about 80 per cent of the land surface, the balance being accounted for by forests, built-up areas, roads, etc.

The mountain and heath areas are nonplowable and markedly deficient in most nutrients, notably calcium and phosphorus. Even so, they can normally carry in summer more stock than can be fed off the lower ground during the winter months. The problems of improving such land are in the first place economic rather than technical, and cannot be divorced from the broad problem of utilizing to the best advantage the total supplies of fertilizers available for all classes of land. In New Zealand, spectacular improvements in the grazing value of many hill areas have resulted from the application of phosphate by aerial top dressing and other methods; even so, their experience has been that the application of phosphate to areas where clovers and other legumes are absent is usually a futile waste (Callaghan, 1950). Such problems of the improvement of mountain and heathland in Britain are being investigated, but for present purposes it will be more profitable to confine attention to the arable and grassland areas on which fertilizers are regularly used.

Of the total area devoted to crops and grass in Great Britain, about 60 per cent is in the arable and 40 per cent in the permanent grass category, and about two-thirds of the arable acreage is normally under tillage crops. Between 1939 and 1946 about 6 million acres of permanent grass were converted to arable production. Table II gives for a few of the principal crops grown in Britain estimated average yields per acre for the three years 1947 (a drought year), 1948, and 1949, and for the ten-year period 1930–1939.

These average yield data suffer from the disadvantage that they are the estimated means of high acreage outputs from the good loams and clays of the eastern half of the country and the relatively low outputs of the climatically less favored and often shallow soils of the marginal and upland districts. They serve, however, to illustrate the over-all production pictures prewar and postwar, and to underline the ultimate dependence of yield on some limiting factor beyond the control of the farmer, as, for instance, the effect of low rainfall on most crops in 1947. Even in a volume such as this which is primarily concerned with phos-

TABLE II

ESTIMATED AVERAGE YIELDS OF THE PRINCIPAL CROPS IN BRITAIN

Crop	Average yields per acre							
	1937		1948		1939		10 years 1930–1939	
	Cwt.[a]	Bushels[b]	Cwt.	Bushels	Cwt.	Bushels	Cwt.	Bushels
Wheat (grain)	15.4	28.7	20.7	38.6	22.5	42.0	17.9	33.4
Barley (grain)	15.7	36.6	19.5	45.5	20.7	48.3	16.4	38.3
Oats (grain)	15.2	53.2	17.8	62.3	18.4	64.4	16.2	56.7
Potatoes	116	217	152	284	138	258	134	250
Turnips and swedes	256	478	294	549	286	534	264	493
Mangolds	320	597	422	788	390	728	365	681
Sugar beet (washed roots)	152	284	210	392	190	355	176	329
		Tons[c]		Tons		Tons		Tons
Seeds hay	28.0	1.57	29.2	1.64	29.9	1.67	28.3	1.58
Meadow hay	21.3	1.19	22.0	1.23	21.2	1.19	21.0	1.18

[a] 1 cwt. = 112 lb.

[b] Bushel equivalents calculated on the following basis: 60 lb. wheat, 48 lb. barley, 32 lb. oats, and 60 lb. each for potatoes, turnips, mangolds, and sugar beet.

[c] 1 ton = 2000 lb.

phorus, it is perhaps not superfluous to remind ourselves of the importance of limiting factors and of the interaction effects of growth factors in both practical and experimental agriculture.

2. *Fertilizer Consumption*

Interaction effects are, of course, of recognized importance in the field of plant nutrition, and the problems of phosphorus consumption and utilization are closely linked with those of nitrogen, potassium, and other nutrients. A fair comparison of the agricultural utilization of fertilizers on any regional basis is possible only when the total quantities consumed are related to the respective areas of land on which they are used. An indication of developments and trends in the use of fertilizers in Great Britain is given by the figures in Table III (Crowther, 1948).

The figures in Table III show that the main differences between prewar and postwar use of fertilizers in Britain are a doubling of the rate of application of nitrogen and a 50 per cent increase in the rate of application of phosphate. The low potassium figure for 1941 is a reflection of wartime supply difficulties: it should, however, also be noted that, since 1947, there has been a sharp rise in potassium consumption to the 20 pounds per acre level. As in other parts of the world, the ratio

TABLE III

AVERAGE RATE OF FERTILIZER APPLICATIONS IN BRITAIN

	Pounds per arable acre			*Plant food ratios*		
	N	P_2O_5	K_2O	N	P_2O_5	K_2O
1939	10.1	29.1	13.4	1.0	2.9	1.3
1941	17.9	32.5	6.7	1.0	1.8	0.4
1947	20.2	42.6	14.6	1.0	2.1	0.7

in which the various plant foods are applied in fertilizers is partly the result of the application of experimental findings to farming practice, partly a reflection of raw material resources, and partly a natural corollary of the system of farming practiced most widely. In British farming, for instance, the keeping of livestock and the application of farmyard manure to the land are traditional. The potassium status of the extensively occurring, pedologically immature, glacial drift soils is reasonably satisfactory, particularly in contrast to a relatively low natural phosphorus status. Consideration of these factors leads to the conclusion that, with such obvious exceptions as texturally light or calcareous soils and areas of intensive crop production, a plant food ratio in fertilizers of 1:2:1 is probably a fair indication of the national average requirement. One further consideration of special importance to all phosphorus fertilization problems is that of calcium status. Despite a marked intensification of liming in the past fifteen years, the great majority of British soils still fall into the too acid or lime-deficient category.

As in other parts of the world, there has also been considerable discussion in Britain on the question of whether farmers should purchase their fertilizers as "straights" or as "mixtures or compounds." Before World War II the farmer had the choice of a confusingly excessive number of "compounds." Although the war did much to hasten the standardization of fertilizer mixtures and to focus attention on the special needs of individual soils and crops, the average British farmer, unlike his Danish counterpart, who thinks mainly in terms of straight fertilizers, is still "compound" conscious; he regards the use of NPK mixtures both as an important labor-saving device and as an insurance premium against the risk of general nutrient deficiency. At present, some two-thirds of the fertilizers used are in the form of compounds. Of the total phosphate used in the country by far the greatest proportion (over 60 per cent) is in the form of superphosphate, with basic slag and ground mineral phosphate constituting the bulk of the remainder. The superphosphate commonly produced is one containing the

equivalent of 18 per cent water-soluble P_2O_5 and with calcium sulphate constituting about half of the weight of the product. In the season 1948–1949 the total production of superphosphate was 1.13 million tons, about three times the 1938–1939 figure. In the same year output of basic slag reached 645,000 tons, an increase of nearly 60 per cent on prewar production; production of "compounds" rose from 650,000 tons in 1938–1939 to 1.9 million tons in 1948–1949 (Commonwealth Economic Committee, 1950).

II. Efficiency of Applied Phosphate

1. Order of Response to Phosphorus in Field Experiments

The influence of climate, farmyard manure supplies, and various other factors affecting response to fertilizers have been summarized by Crowther and Yates (1941) and by Crowther (1948), in most valuable publications covering the results of all the principal field experiments carried out in Great Britain during the present century.

Weather conditions, especially rainfall, have an important influence on the fertilizer requirements of soils and crops. High rainfall favors vegetative growth, delays ripening, and so reduces the need for nitrogen supplements. To hasten ripening more phosphate is necessary, and extra phosphate is also needed against the fact that the leaching rate of lime is greater in the soils of high-rainfall areas. Crowther and Yates (1941) show, for instance, that average responses to phosphate in the south and east of England are only about two-thirds those in central and north England. In Scotland, Wales, and the west of England, on the other hand, average responses to phosphate are about 1⅔ times as great as those in central and north England. Pedological and temperature differences are of course operative over these regions, but broadly these differences in average response correspond to differences in annual rainfall ranging from some 25 inches (640 mm.) in southeast England to such figures as 30 inches on the east coast of Scotland and rising to from 60 to 70 and over in the wetter western regions. Generally the rainfall in Britain is more or less evenly distributed throughout the year.

Another finding, to which attention was drawn by Crowther and Yates and which rather surprised most British farmers, concerns the effect of dressings of farmyard manure on fertilizer response. Average results from the analyses of large numbers of samples indicate that 10 tons dung will contain about 110 pounds N, 55 pounds P_2O_5, and 110 pounds K_2O. The fertilizer value of dung cannot, however, be regarded as equivalent to fertilizers supplying these amounts of plant food. Contrary to widespread belief in Britain, the application of dung does

not materially affect the need for nitrogen. It does, however, reduce by about one half the response to phosphate and by about two-thirds the response to potash normally obtained on undunged land of average fertility. This finding, when related to average crop response data, implies that in the presence of a 10-ton dressing of farmyard manure, fertilizer dressings should be reduced by the equivalent of about 45 pounds P_2O_5 and 65 pounds K_2O (Crowther, 1948). These negative interaction effects between dung and phosphate and dung and potash are of obvious importance in practical agriculture. Although it would be interesting to pursue in greater detail both the theoretical and the practical implications of these results, for present purposes we merely note the finding as being an integral part of the general picture of fertilizer response in Great Britain.

Of the crops commonly grown in Britain, swedes and turnips are relatively the most responsive to phosphate. Swedes, for instance, show average responses of the order of 20 per cent increase in yield in the southeast of England and 50 per cent and over in the north of Scotland. Potatoes and mangolds come next, and sugar beet is generally the least responsive to phosphate of the common root crops. Cereals usually give small percentage responses to phosphate except in markedly deficient soils; but grasses and clovers respond markedly, and, in cereal crops which are being undersown with grass and clover seeds, the practice commonly adopted for pasture establishment, the emphasis is, of course, on meeting the requirements of the undersown crop.

2. Relative Effectiveness of Phosphate in Different Forms

The soils of the major part of the British Isles north of the Thames valley have been derived in the main from glacial drifts of widely varying geological composition. Most of our Macaulay Institute work, for instance, has been done on soils from such diverse parent material groups as Acid Igneous, Medium and Basic Igneous, Medium and Basic Sedimentary, Acidic Sedimentary, Water-Sorted Sediments, and Siliceous Deposits. The great majority of these soils are acid with pH values 5 to 5.5 and exchangeable calcium contents of the order of 4 to 5 m.e. per 100 grams. On these soils the order of the response to phosphate commonly obtained with a phosphate-responsive crop, turnips or swedes, as judged by the mean yields obtained in numerous field experiments carried out in recent years, is briefly as follows: At the 10 ton per acre level of yield in the absence of phosphate, the average responses to superphosphate in the absence of dung are 5, 7, and 8 tons roots per acre from dressings of 40, 80, and 120 pounds P_2O_5 respectively. Farmyard manure has the effects (1) of raising the mean yield

in the absence of phosphate from about 10 to 16 tons roots per acre, and (2) of reducing by about half the above average responses.

During the past ten to twelve years, we have included in our field experiment program most of the phosphates in common use and several of the more recent experimental products, e.g., various high-temperature phosphates including *silicophosphate*, T.V.A. calcium metaphosphate coprolite, *nitrophosphate*, reverted superphosphates, and phosphates in granular and powdered forms. Williams and Reith (1948) have summarized the results of a considerable number of field and pot experiments with such materials, and the implications of these and other results have been discussed in subsequent publications (Stewart, 1950; Stewart, 1951; Williams, 1951; Reith, 1951). During the war years, the British Ministry of Supply sponsored a joint investigation by the Building Research Station and the Rothamsted Experimental Station on the production and agricultural value of silicophosphate fertilizers, but so far the results of this work have been issued only in a publication under Crown Copyright (Monograph 11.108, January 1951). This investigation was concerned primarily with the possibility of making phosphatic fertilizers by high-temperature processes not requiring the use of sulfuric acid. The initial experiments were based on the German Rhenania phosphate—a mixture of dicalcium sodium phosphate ($2CaO$, Na_2O, P_2O_5) and dicalcium silicate ($2CaO$, SiO_2).

In the experiments described by Williams and Reith (1948) there are no striking or consistent differences in the effectiveness of the different phosphates other than mineral phosphate, calcium metaphosphate, and Semsol (a superphosphate-mineral phosphate mixture); the latter forms tended to be generally inferior, although frequently effective on turnips and swedes but not on potatoes. With grasses and clovers in pasture reseeding experiments, similar results to those for turnips and swedes were obtained.

From these and other current experiments on such responsive crops as turnips, swedes, and pasture, our broad conclusion is that phosphorus fertilizers having 70 per cent or more of their phosphorus soluble in 2 per cent citric acid are as effective as superphosphate in acid soils. This group includes dicalcium phosphate, disodium phosphate, various high-teperature phosphates of the silicophosphate type described by Crowther and Lea (1946), reverted superphosphates, ammoniated superphosphate, steamed bone flour, and basic slag. From both the Rothamsted and the Macaulay work, the general indications are that basic materials such as silicophosphates and basic slags are likely to be at least equally as effective as superphosphate on acid soils and slightly less effective than superphosphate on neutral soils. For practical pur-

poses we regard silicophosphates as being closely akin to basic slags of high citric acid solubility. Such phosphorus compounds as ground mineral phosphate, bone meal, coprolite, calcium metaphosphate, and others in the general group of those having appreciably less than 70 per cent of their phosphorus soluble in citric acid, are usually less effective than superphosphate. On turnips, swedes, and pasture, especially on acid soils, the differences are normally small, of the order of 5 per cent, but, with potatoes, it is our experience that all forms of phosphate of low citric acid solubility are relatively ineffective.

These observations apply primarily to the first-year or immediate effects of the various phosphorus supplements. Unfortunately there have been relatively few field experiments designed to measure accurately the residual effects of earlier dressings. It is our general experience, however, that a phosphate which has been inferior in immediate effects has also remained inferior in its residual effects. This has been well established, for instance, with basic slags, for which the citric acid solubility test is a sound criterion of fertilizer value. Basic slags of low citric acid solubility have, practically without exception, been inferior to those of high citric acid solubility both in immediate and residual effects.

The results of these British experiments with different forms of phosphate can usefully be considered from two viewpoints. On the one hand, we can regard the results as being in the nature of a worthy testimonial to superphosphate, leading to the broad conclusion that no other form of phosphate is consistently superior. Hence the greatest compliment which we might pay to a phosphatic fertilizer is to say that it appears to be as good as superphosphate. It may be, of course, that some of the virtue of superphosphate is due to the calcium sulfate which it contains and which undoubtedly influences the physical properties of the product. Indeed the absence of obvious signs of sulfur shortage in British arable soils may well be due in some measure to widespread use of superphosphate and incidental application of calcium sulfate. Even so, it is clear that water solubility of phosphate is a good criterion of fertilizer value. But, in contrast to this, it is equally true to say that there are many forms of phosphate which are not water-soluble but which are nevertheless of high fertilizer value. In this particular respect, therefore, the British regulations governing the sale of fertilizers (Fertilizers and Feeding Stuffs Act 1926), according to which a phosphate is either "water-soluble" or "insoluble," have outlived their usefulness. The authorities in Britain are meantime giving very serious consideration to the problem of amending these particular regulations. In this general connection considerable interest naturally attaches to the am-

monium citrate and other methods of evaluating phosphorus fertilizers which are being used in the United States. As already indicated, British experience has been that solubility in 2 per cent citric acid is a very useful method of assessing the phosphorus value of a considerable range of phosphatic fertilizers.

In addition to experiments on different chemical forms of phosphorus, a certain amount of field work has also been undertaken with phosphatic and other fertilizers in granular and powdered forms. The amount of experimental work as yet undertaken on this subject in Britain is insufficient to permit firm conclusions to be drawn; in particular, further experiments are required covering a wider range of particle size. In the light of present knowledge, the position is adequately summarized in the recent summary report by Sherman and Hardesty (1950). From the experiments which we have carried out so far, all that we can say is that phosphates in granular form are at least as effective as those in powder form. In many of the experiments the trend has been in favor of the granular products, but we have not had results so strikingly in favor of granulation as those reported, for instance, from Sweden. Granular products have many obvious advantages over powder forms; they are more convenient to store, handle, and distribute, and they are specially suitable for drilling, where regularity of flow is so important. From the angle of phosphate fixation there are of course theoretical considerations in favor of granules, which can be penetrated by plant roots but which expose less surface to the soil than do powders. In Britain probably about two-thirds of the fertilizer mixtures used are in granular forms. It is probably fair to say that their popularity initially was based mainly on considerations of their superior physical condition, and that it was merely strengthened subsequently by the finding that they are invariably equal, and sometimes superior, to the powder forms.

3. Phosphate Fixation

The general problems of fixation and availability emerging from our experimental work on the phosphate relationships of soils have been outlined in recent publications (Williams, 1949; Williams, 1950). The availability to plants of the various phosphorus compounds in a soil depends primarily on the concentration of phosphates in the soil solution over a period of time, i.e., the degree of solubility of the compound and the rate at which it dissolves are both of primary importance. The actual uptake of phosphate by a plant, and hence availability as reflected by the ultimate yield and composition of the crop, depends, however, on factors other than primary solubility. It depends, for instance,

on such factors as the supply and balance of other nutrients and the aeration and structure of the soil. Since availability and solubility are not synonymous, we prefer to use the word fixation merely as a convenient term to denote decrease in solubility, i.e., in the same general sense as that outlined by Dean (1949), who has defined fixed phosphorus as the soil phosphorus which has become attached to the solid phase of soils. The next stage is to try to identify the various ways in which conversion to less soluble forms may take place and to distinguish, for instance, between fixation in forms likely to become readily available as a source of plant food as contrasted with fixation in difficultly available forms.

The general problems of the retention of phosphate by soil have received the attention of numerous investigators. In a recent review Wild (1950), for instance, has summarized the general views expressed in no fewer than 162 papers by workers in different parts of the world. No attempt will be made, therefore, in the present paper to do more than indicate a few general aspects of the problems involved. Williams has summarized the main reactions involved in the fixation of phosphate by soils under the heads of biological fixation, and physical and chemical fixation. Under the latter head come precipitation by iron, aluminum, and calcium, and sorption, covering adsorption, absorption, and chemisorption and including anion exchange. From one-third to one-half of the total phosphate in our ordinary mineral soils is present in organic form, but this aspect of the subject, which has been so usefully reviewed by Pierre (1948), has been little investigated in Britain. Most of our work so far has been concentrated on the inorganic fraction, and particularly on rate of fixation and its significance in regard to phosphate availability.

It is very difficult to establish with certainty under field conditions the time necessary for more or less complete fixation to take place. From the data so far available from field and pot measurements of the availability of superphosphate residues, supplemented by solubility data on rate of fixation in moderately acid soils (Williams and Stewart, 1943), it appears that there are two main stages in the fixation. In the first stage, the superphosphate rapidly loses its identity and the dominant reaction is probably an exchange adsorption. This freshly adsorbed phosphate is much less soluble than superphosphate, but it is still an effective plant nutrient and, under fallow soil conditions, appears to remain so for several months. Secondary physical and chemical changes, constituting the second stage, take place in the course of a year in cropped soils, and these changes appear to reduce the inherent availability of the phosphate to plants by as much as 50 per cent. Even so,

the residues still appear to be of some value to plants. Comparison of the results of field and pot experiments indicates that, in many instances, the low direct residual effects of superphosphate in the field may not be entirely attributable to fixation of phosphate in unavailable form. Although this is undoubtedly a dominant factor, reduction in the positional availability and concentration of the residues is also a factor of importance.

There is still much to be learned about the residual effects of phosphorus fertilizers under differing climatic, soil, and cropping conditions. That immediate or first season's effects of even light dressings can often be spectacular and that the direct residual effects of even relatively heavy dressings are generally low is fairly common experience. Williams (1950), for instance, has given the results of a few experiments undertaken to measure the residual effects of relatively heavy dressings of superphosphate at rates supplying the equivalents of approximately 200 pounds and 500 pounds P_2O_5 per acre, respectively. The results show that these dressings did have very considerable residual effects in the 12- to 24-month period and appreciable residual effects in the 24- to 36-month period following application. But the most striking feature of the results is the fact that, with phosphate-responsive crops of turnips and swedes, the residues after even only one year had much lower fertilizer values than that of a fresh dressing of 600 to 700 pounds superphosphate per acre applied to the crop. The results indicate that the residues of the 500 pound per acre dressings in the 12- to 24-month period following application are roughly equivalent in effect to only 80 to 100 pounds P_2O_5 applied as a fresh dressing.

We have little accurate information on the ultimate value over a long period of phosphate which has been subjected to fixation, redistribution by cultivation, and aging in the soil. The value of accumulated phosphate residues in practical agriculture will almost certainly depend on husbandry systems, on the liming of acid soils, on the maintenance of the supplies of other nutrients, and on other factors. There appears, for instance, to be some evidence that the application of fresh dressings of phosphate may help the plant to utilize phosphate reserves in the soil more fully, and there are many instances of positive interaction effects between the main nutrients. Recent work, however, in Sweden (Eriksson, 1942; Mattson *et al.*, 1949; Mattson *et al.*, 1950) has shown that salts increase the sorption of phosphate by acid soils and, according to the theory developed by Mattson, the resultant effect on phosphate uptake by the plant may be either positive or negative, depending on such factors as the cation exchange capacities of the root acidoids and the soil colloids, and the salt concentration. The possible

importance of such effects in normal practice, however, remains to be clarified.

In the course of our general experimental work on phosphate problems we have frequently observed that the direct residual effects of phosphate dressings are considerably greater in soils derived from Old Red Sandstone than in those of granitic origin. We do not know yet why this should be so; in our field experiment work on fertilizer problems in crop production we are, however, regularly following the plan of locating our field experiment centers on contrasting soil associations or series which have been identified by our soil surveyors. We hope in this way gradually to accumulate more accurate information on the interrelationships of productivity and soil type and, in particular, on the relationship between phosphate availability and fertilizer response and soil parent material and other pedological factors. In this particular field there are many gaps in our British knowledge.

These particular aspects of the general problems of phosphate fixation and availability, and their significance in relation to the immediate and residual effects of phosphorus supplements serve to illustrate the broad method of approach which we have been adopting in our field, pot, and laboratory experiment work. The evaluation of the phosphorus status of soils has been discussed by Williams (1952) in a recent review. Although much has been done in recent years to clarify understanding of the nature, solubility relationships, availability, and extraction of different categories of phosphorus, we do not think that conventional laboratory methods can yet be expected to give more than a general indication of the ability of a soil to meet the phosphorus requirements of crops. The field experiment still remains the criterion, and the usefulness of individual extraction methods must be judged by the correlation obtained with the results of field experiments covering appropriate climatic conditions, soil types, crops, and agricultural practices. More recent work on the interrelations of various readily soluble phosphorus values and crop responses for different soils indicates, for instance, that the value of a particular extractant as diagnostic aid varies with parent material and other pedological factors (Williams, Reith, and Inkson, 1952).

The phosphorus field is undoubtedly a fruitful one for anyone wishing to speculate or theorize. From what has been said with particular reference to mainly acid soils of glacial drift origin in Britain, it will be clear that there are too many gaps in our knowledge of these to permit of further useful speculation at this stage. Instead, an attempt will be made to point to some of the implications of the work to date in British farming practice.

4. *Rates and Time of Application*

From what has been said on the relative effectiveness of phosphate in different forms, it is clear that superphosphate is not easily surpassed and that no major increase in the efficiency of applied phosphate is likely from the use of such other forms as we have so far tested. This does not mean of course that alternative sources of phosphate cannot be used to excellent advantage. The point to be underlined is that, in our opinion, British agriculture must concentrate on other methods of increasing the effectiveness of all phosphorus supplements, rather than sit back and hope for startling benefits to accrue from some entirely new form with intrinsically superior properties. It has long been the practice of many British farmers to pin their faith on the application of single, relatively heavy dressings of phosphate at intervals of a few years, in the general and rather pious hope that they were thereby creating a useful working reserve of phosphate in the soil. The number of farmers in this category has shown a steady decline in recent years. The impact of science on agriculture is undoubtedly responsible for this to some extent; but most scientists will agree that the change in outlook is probably due in even greater measure to the impact of changing economic conditions enhancing the raw material value of phosphorus, sulfur, and other fertilizer components. We have seen that fixation of added phosphate in relatively unavailable forms in the soil is much less serious in the first than in the second and subsequent years. The law of diminishing returns applies in full measure to the addition of phosphorus supplements to the soil, and the steeply rising form of the normal phosphorus-response curve is well recognized. The acid glacial drift soils so typical of most of Britain are phosphate-responsive and, under these conditions, any attempt to build up quickly, by means of heavy applications, reserves of phosphate in the soil in the hope that they will last for years is fundamentally unsound and uneconomic. The frequent or annual application of phosphate according to the responsiveness of individual crops, with suitable adjustments for local soil and climatic conditions, is undoubtedly the sounder practice. This in essence is what we advise our farmers to do. As regards time of application of phosphate to tillage crops, the safest plan is to give the dressing just ahead of, or at the time of, seeding, so as to reduce to a minimum the amount of fixation likely to take place before the young plants are able to start using it. From the limited amount of experiment work which we have done on the question of time of application of phosphates to various crops, our conclusion is that, particularly in texturally heavy soils and in soils of low organic matter content, there may be a reduc-

tion in efficiency if superphosphate is applied 3 to 4 months ahead of seeding. With the less soluble phosphates such as ground mineral phosphate, application ahead of seeding is not likely to be disadvantageous and, on grassland, application of phosphate in any form is probably best undertaken a few months ahead of the commencement of spring growth.

5. *Method of Application*

The first superphosphate produced by Lawes at Rothamsted over a century ago was applied by placing it in drills or rows along with the seed. This appeared to work quite well; however, when Lawes extended his work to include nitrogenous fertilizers, he observed that when these were placed in bands or rows they frequently had a harmful effect on germination. It was this latter observation that really led to the general adoption of broadcasting as the standard method of applying fertilizers. Although many of our shrewd and imaginative Victorian farmers tried out from time to time new ways of applying fertilizers, including such ingenious devices as a "3 horse machine sowing 4 drills with a slurry of superphosphate which was joined in the delivery spout by a trickle of turnip seed" (*Cunningham*, 1951), the broadcast method held the field in Britain more or less unchallenged for a hundred years.

Wartime conditions made imperative the greatest possible economies in both materials and labor, and this led to a large volume of work being undertaken on methods of fertilizer application. With cereals (Crowther, 1945; Stewart and Reith, 1945; Reith, 1952), a crop which is not particularly responsive to phosphate, experiments on the combine-drilling of fertilizer with the seed, both in the south of England and in the north of Scotland, have shown that if superphosphate is drilled with the seed, only half as much is required to give the same increase in yield as when the superphosphate is broadcast. From the point of view of practical agriculture, this is a far more spectacular and promising finding than has emerged from most other work to date on means of increasing the effectiveness of applied phosphate. We have, of course, had to remind our farmers that equally promising results from contact placement have not been obtained with all crops and all fertilizers (Stewart, 1949). Under British conditions, germination and establishment of cereals may be adversely affected if more than the equivalent of about 30 pounds N and 60 pounds K_2O per acre are combine-drilled with the seed; but mixtures containing up to these amounts are usually more effective combine-drilled than broadcast.

The Rothamsted and Macaulay work on fertilizer placement has been greatly facilitated by close collaboration with the National In-

stitute of Agricultural Engineering (Cooke, 1947; Cooke, 1949a), who have turned out for us special experimental machines, enabling fertilizers to be placed in different positions relative to the seed (Cooke, 1951). Although it is too early yet to give specific alternative recommendations to the customary broadcast method of applying fertilizers for individual British crops, it is clear from the preliminary results that, in many cases, band placement of fertilizers, either below or below and to the side of the seed, may be superior to broadcast application. This applies particularly to such crops as peas, which have a relatively small root system and which mature quickly. For instance, in the Rothamsted work (Crowther, 1949), a PK mixture gave 2 cwt. (approximately 4 bushels) more threshed peas per acre when placed in side bands than when broadcast. With other crops less promising results have been obtained; sugar beet and mangolds, for instance, are very sensitive to injury to germination by soluble fertilizers placed in contact with the seed. Side-band placement, however, generally favors the early establishment and growth of most crops (Lewis, 1941), but it is doubtful whether this justifies the purchase of special drills for moderate acreages of individual crops. An alternative procedure, which has given good results in several experiments, is to plow down broadcast dressings of P or PK fertilizers and to follow this by surface dressings of nitrogen at a time to suit the individual crop.

The general importance of the factor of positional availability of a fertilizer supplement in the soil, and its dependence on the cultivation methods normally employed are well illustrated by the results of placement experiments with various fertilizer mixtures on potatoes in Britain (Cooke, 1949b; Stewart, 1949). We were familiar with the promising results of the American work on band placement for potatoes as described, for instance, by Cumings and Houghland (1939), and we were interested to see whether the same held good under British conditions. By far the greater proportion of the potato acreage in Britain is still grown under a cultivation system which involves double ridging, i.e., first the opening of ridges or planting furrows followed by the splitting back of these ridges to cover the seed, the normal spacings being 27 inches row width and 8 to 10 inches between the seed tubers in the row. A comparison was therefore made of broadcasting before the initial ridging and broadcasting after the first ridging alongside various contact and side placements in bands. The results (Cooke, 1949b) showed that 2 parts of fertilizer applied broadcast after the initial ridging gave as good yields as 3 parts fertilizer broadcast before the first ridging. Apart from this, there were practically no differences in yield attributable to the method of applying the fertilizer, except in very dry

seasons when some damage resulted from the application of relatively heavy dressings in bands in contact with the seed tubers. Under this system of growing potatoes, broadcasting immediately before planting is a perfectly sound practice and there is nothing to be gained by any more elaborate method of applying the fertilizer.

In the past few years there has been a considerable increase in the acreage of potatoes grown with the aid of planting machines working on the flat, a system in which the potatoes are planted and covered by a ridge in one operation. A few but by no means all of these machines have fertilizer-distributing attachments. The likely extension of their use in agriculture, with consequent tendency to abandon gradually the traditional double ridging system, has refocussed attention on the placement problem for potatoes. Preliminary results, as yet unpublished by G. W. Cooke at Rothamsted, are in general agreement with those obtained in the American work and with theoretical expectation based on considerations of the positional availability in the soil of fertilizer particles following application in different ways.

Even within the relatively small confines of Britain, the cultural operations normally practiced by farmers in different parts of the country vary considerably. In the south of England, for instance, sugar beet is invariably grown on the flat, whereas under the cooler, moister conditions obtaining in Scotland ridges are favored and are indeed traditional for most root crops. These differences in cultural operations are based on the consideration of such various factors as the need for ready means of weed control, the removal of excess moisture in wet periods, and the conservation of moisture in the seed bed. Originally too, ridging enabled the all important farmyard manure to be concentrated in the root zone, and considered from the angle of the positional availability of fertilizer supplements, broadcasting and ridging together constitute a quite effective form of placement. By means of a specially constructed root drill, we are meantime investigating placement possibilities with turnips and swedes grown in ridges. Preliminary results indicate that, even under a ridge system of cultivation, placement of superphosphate in a band 1½ to 2½ inches below the seed is likely to be more effective than either broadcast application or placement in bands in other positions relative to the seed. Although we require much more information on the relative effectiveness of different methods of applying fertilizers under varying conditions of soil, crop, and season, we do feel that the factor of positional availability in the soil is one of prime importance in so far as the efficient utilization of fertilizer phosphorus is concerned. It may well be, therefore, that in the future our farmers will have to think less in terms of applying complete fertilizer mixtures, as they

prefer to do at present, and more in terms of placing phosphorus and potassium and of applying readily soluble nitrogen separately, according to the requirements of individual crops and soils. The translation into practice of the results even of those experiments which have given quite conclusive results is complicated, of course, by considerations of the extra labor, and frequently also of equipment, involved in the separate application of simpler mixtures or straight fertilizers.

6. Lime and Phosphate

The agricultural liming pendulum in Britain swung from a point of reasonably adequate liming in the second half of last century to the extreme of definite underliming in the middle thirties of the present century. The introduction of Government Land Fertility and Agricultural Lime Schemes in 1937 undoubtedly did much to reawaken interest in liming; but even with the vastly increased consumption during recent years, the annual total at present being applied works out at the equivalent of about 200 pounds CaO per arable acre, which is barely a maintenance requirement. Lime can operate in so many different ways in the improvement of acid soils that it is exceedingly difficult to isolate and assess the value of its numerous component effects. On the phosphate fixation side, we think it important to note that sorption fixation decreases rapidly at higher pH values in the region of 6 and over. Similarly the calcium phosphates, which may be formed by precipitation in slightly acid to neutral soils, fall into the readily available category. On the specific issue of the effect of lime on the effectiveness of applied phosphate, there is a considerable amount of evidence that liming an acid soil to a pH of about 6.5 does increase the effectiveness of superphosphate. An illustration of this effect from our own work is provided, for instance, by data on the yield and composition of crops from a series of long-term experiments on the relative effectiveness of different liming materials described by Reith and Williams (1949). At one center the yield of mangolds was increased almost sevenfold and, at the same time, the phosphorus content of the roots was nearly doubled by liming. In terms of total P_2O_5 removed from the soil, this corresponded to 2.1 pounds per acre, in the absence of lime and 24.3 pounds per acre in the presence of lime. The percentage increases in the phosphorus contents of other crops were less pronounced but still positive, and the total phosphorus removed in the first four rotation crops, mangolds, barley, barley, and hay amounted in the absence and presence of lime to 33.5 and 90.4 pounds. P_2O_5 per acre, respectively. Quite apart from the effect of calcium on phosphorus uptake by crop plants, such figures as these serve to underline the important practical

point of the need for adequate replacement fertilizing when yields are increased following the introduction of specific remedial measures. As far as the extensive acreages of acid soils in Britain are concerned, it is doubtful whether any single measure could do more than judicious liming to increase productivity and, at the same time, keep as much as possible of the soil phosphate in active circulation.

There is one other aspect of the liming problem, or rather of the liming problem in reverse, which has been interesting us lately. In routine determinations of the readily soluble phosphorus contents of soils as a guide to phosphate requirements, we customarily use acetic acid (2.5 per cent by volume) as an extractant. We thought that it would be interesting in a particular set of experiments to remove some of the acetic acid-soluble phosphorus and then study the solubility and availability of the phosphate remaining in the treated soils. Parallel experiments with 0.007 *N* H_2SO_4 as an extractant were also undertaken. Williams (1951b) has described the results obtained with soils derived from Basic Igneous, Old Red Sandstone, Slate, and Granitic parent materials, respectively, and has pointed out that, not surprisingly, the effect of removing relatively small amounts of readily soluble phosphate was completely obscured by other effects of the acid treatment. Pot tests with oats showed that extraction with either acetic acid or dilute sulfuric acid as above, followed by restoration of pH and of cation content, increased greatly the availability of the remaining phosphate. This more than compensated for the readily soluble phosphorus removed and was reflected both in higher yields and higher phosphorus uptakes. Neubauer determinations and solubility measurements in water and in salt solutions also gave higher values for the treated soils.

The increases in solubility run parallel to, and are probably sufficient to account for, the increases in availability. Williams (1951b) has discussed the nature of the effect, and has attributed it to a combination of such factors as deactivation of fixing agents, partial hydrolysis of difficultly soluble inorganic and organic phosphates, and redistribution of phosphate in the soils. These acid treatments are, of course, much more drastic than any treatment likely to be encountered in agricultural practice, even where heavy dressings of ammonium sulfate, sulfur, or sulfuric acid sprays are used. It is interesting to speculate, however, on the implications of such results on the changes to be expected in soil phosphate with increasing soil acidity, the low availability of phosphate in acid soils, and the beneficial effects of liming. Pretreatment with acid must cause a drastic change in a system in which there has been gradually established a stable equilibrium. Is there a correspond-

ing though probably less drastic reverse change from the stable equilibrium condition when lime is applied to an acid soil?

7. *Other Factors Influencing Efficiency of Applied Phosphate*

Reference has already been made to the effect of dung in reducing responses to phosphorus and potassium but not nitrogen. These effects are undoubtedly associated with microbial activity and hence there is uncertainty regarding the period during which the nutrients present become available to plants; they cannot, therefore, be assessed solely in terms of the N, P, K contents of the organic supplement. Although it is virtually impossible to evaluate the individual contributions of the component chemical, physical, and biological factors involved in the improvement of soil productivity when dung is applied to particular soils, there seems to be little doubt that one of its net, long-term effects is to promote the better utilization of both native and applied phosphate. We have been interested in the experimental work undertaken especially in Sweden and America on the apparent advantages of mixing superphosphate with dung before applying it to the land, and we have in hand a number of long-term, factorial, dung-NPK experiments covering this and similar treatments. Although the preliminary results are promising, we are not yet at the stage of drawing conclusions as to the efficacy and general practicability of such a procedure in farming practice. One has indeed only to glance through a collection of papers such as those in the August 1949 issue of *Soil Science*, to see how complex are the problems of the utilization of phosphorus in various inorganic and organic forms by different crops, and how urgent is the need to fill outstanding gaps in knowledge before attempting generalizations.

III. Conclusions

Against the background of land utilization, fertilizer consumption, and general response to phosphate under varying climatic, soil, and cropping conditions encountered in British farming practice, an attempt has been made in this chapter to present our views on such questions as: the relative merits of phosphate in different forms and the unlikelihood of spectacular increases in effectiveness from the introduction of new or modified chemical forms of fertilizer phosphorus; the advantages of frequent dressings at moderate rates as contrasted with infrequent heavy dressings; the importance of the factor of positional availability of phosphorus supplements in the soil and the consequent need for keeping methods of fertilizer application under constant review; the importance of adequate liming of acid soils and the likely role of de-

composing organic matter in helping to keep as much as possible of the soil phosphate in active circulation. An outline has also been given of our views on the broad problems of the fixation of phosphate in soil. Although the direct residual effects of phosphorus supplements after they have been in the soil for a year or more are generally low, spectacular yield increases normally follow the application of even relatively light dressings to phosphate-deficient, acid soils. Further, the response to such supplements does obey the general law of diminishing returns. Cunningham (1951) has pointed out that in Great Britain we are applying annually about 166,000 tons of phosphorus and accounting for only half of this as coming off the land. On the one hand, this may be regarded as a measure of inefficiency of present methods, but against this, we would undoubtedly suffer if we stopped applying phosphate. To illustrate this, Cunningham has pointed to the involuntary, large-scale experiment in phosphate economy which France had to carry out during the years 1940–1945. By the end of that time phosphorus-deficiency symptoms were everywhere evident in crop yield, and in both crop and animal health. There appears to be no escape, therefore, from continuing applications of phosphorus if production and health are to be maintained at reasonable levels.

In considering the efficient utilization of phosphorus as a fertilizer, we think that it is of the utmost importance to remember that, although the direct residual effects even of heavy dressings are invariably low, the indirect residual effects of even light dressings may be appreciable. In this connection good farm management, involving the simultaneous application in practice of all the principles of good husbandry, is of undoubted importance. We have had striking illustrations of one of these phases of good management in our work on the improvement of old worn-out pastures by plowing, liming, manuring, and reseeding. The differences in early establishment between plots with no phosphate and plots receiving even a modest 40 pounds P_2O_5 per acre dressing were indeed striking. In British farming practice it has long been accepted as a maxim that good pasture is a sound basis of fertility, and such was the case in these reseeding experiments. The well established pastures in the lightly phosphated plots continued to keep ahead of their phosphate-deficient neighbors; they had a greater stock-carrying capacity and, as a result, got more dung and urine to help them along and so, in the general sense, were enabled to build up fertility. Cumulative effects of this type, resulting from the application of even light fertilizer dressings coupled with good management, are of obvious importance, particularly where, as in most of the west and north of Britain, rotation pasture is an important factor in the maintenance and

improvement of fertility. Now for the poor management side of the story. Good pasture management in the region in which these experiments were carried out involves the control of grazing at certain times of the year and the prevention, so far as possible, of the development of stemmy growth and the emergence of flowering heads, particularly during the establishment stages. In these experiments, a heavy dressing of phosphate gave a better take and initial establishment of grasses and clovers than a light phosphate dressing. But the unintentional introduction of a variable management factor ultimately led to plots in which the light phosphate dressing followed by good pasture management gave a better sward than could be found in plots receiving the heavy phosphate dressings coupled with poor or indifferent management. In this particular observation there is surely a lesson not to be ignored in any appreciation of the problems of utilizing fertilizer supplements efficiently.

References

Callaghan, F. R. 1950. 11th Conference Grassland Association, New Zealand.

Commonwealth Economic Committee 1950. A Survey of the Trade in Fertilizers, *34th Report*. H.M.S.O., London.

Cooke, G. W. 1947. Fertilizer placement field work. *Agr. Eng. Rec.* (Natl. Inst. Agr. Eng., England) **1**: 240–244.

Cooke, G. W. 1949a. Fertilizer placement. *Fertilizer Soc. Eng. Proc.* **6**, London.

Cooke, G. W. 1949b. Placement of fertilizer for potatoes. *J. Agr. Sci.* **39**: 96–103.

Cooke, G. W. 1951. The mechanical application of fertilizers in field experiments. *Empire J. Exptl. Agr.* **19**: 160–174.

Crowther, E. M. 1945. Combine drilling of phosphate fertilizers for cereals. *Agriculture (Engl.)* **52**: 170–173.

Crowther, E. M. 1948. Fertilizers during the War and After, Bath and West and Southern Counties Society. Pamphlet No. 13, 2nd ed., Mendip Press Ltd., Bath.

Crowther, E. M. 1949. Soils and fertilizers. *J. Roy. Agr. Soc. Engl.* **110**: 135–148.

Crowther, E. M., and Yates, F. 1941. Fertilizer policy in war time. *Empire J. Exptl. Agr.* **9**: 77–97.

Crowther, E. M., and Lea, F. M. 1946. Silico phosphate. *Agriculture (Engl.)* **53**: 102–105.

Cummings, G. A., and Houghland, G. V. C. 1939. Fertilizer placement for potatoes. *U. S. Dept. Agr. Tech. Bull.* **669**.

Cunningham, H. V. 1951. Fertilizer trends and future prospects. *Advancement of Sci.* **8**: 303–307.

Dean, L. A. 1949. Fixation of soil phosphorus. *Advances in Agron.* **1**: 391.

Eriksson, S. 1942. Untersuchungen über die Einwirkung von Kalisalzen auf die Löslichkeit der Bodenphosphorsäure. *J. Roy. Swed. Acad. Agr.* **81**: 6½.

Lewis, A. H. 1941. The placement of fertilizers. 1. Root crops. *J. Agr. Sci.* **31**: 295–307.

Mattson, S., Eriksson, E., Vahtras, K., and Williams, E. G. 1949. Phosphate relationships of soil and plant. I. Membrane equilibria and phosphate uptake. *Ann. Roy. Agr. Coll. Sweden* **16**: 458–484.

MATTSON, S., WILLIAMS, E. G., ERIKSSON, E., and VAHTRAS, K. 1950. Phosphate relationships of soil and plant. II. Soil-soil solution equilibria and phosphate solubility. *Ann. Roy. Agr. Coll. Sweden* **17**: 64–91.

PIERRE, W. H. 1948. The phosphorus cycle and soil fertility. *J. Am. Soc. Agron.* **40**: 1–14.

REITH, J. W. S. 1951. Factors affecting the methods of applying fertilizers. *Scot. J. Agr.* **31**: 104–109.

REITH, J. W. S. 1952. Fertilizer placement for cereal crops. *Empire J. Exptl. Agr.* **20**: 103–114.

REITH, J. W. S., and WILLIAMS, E. G. 1949. The effectiveness of various liming materials. *Empire J. Exptl. Agr.* **17**: 265–276.

SHERMAN, M. S., and HARDESTY, J. O. 1950. Reviews of experimental work on the agronomic effects of particle size of superphosphate and of mixed fertilizers containing superphosphate or other water-soluble phosphates. *U. S. Dept. Agr. Plant-Food Memorandum, Rept. No. 20.*

STEWART, A. B. 1949. Fertilizer placement for arable crops. Department of Agriculture for Scotland. *Advisory Leaflet No. 3* [n. s.] H.M.S.O., London.

STEWART, A. B. 1950. Fertilizer utilization with special reference to phosphates. *Fertilizer Soc. Engl. Proc.* **12**, London.

STEWART, A. B. 1951. Fertilizers and crop production. Dept. Agr. for Scotland. *Advisory Leaflet No. 18* [n. s.] H.M.S.O., London.

STEWART, A. B., and REITH, J. W. S. 1945. Comparison of broadcast and drill applications of fertilizers. *Scot. J. Agr.* **25**: 167–171.

WILD, A. 1950. The retention of phosphate by soil. A review. *J. Soil Sci.* **1**: 221–238.

WILLIAMS, E. G. 1949. Phosphate fixation. *Natl. Agric. Advisory Service Quart. Rev.* (Great Britain). **1**: 147–155.

WILLIAMS, E. G. 1950. Phosphate fixation and availability. *J. Sci. Food Agr.* **8**: 244–248.

WILLIAMS, E. G. 1951a. Making the best use of phosphate fertilizers. *Scot. J. Agr.* **31**: 68–72.

WILLIAMS, E. G. 1951b. Effects of acid treatment of soils on phosphate availability and solubility. *J. Soil Sci.* **2**: 110–117.

WILLIAMS, E. G. 1952. Evaluating the phosphorus status of soils. *Trans. Intern. Soc. Soil Sci.*, Joint Meeting of Comm. II and IV, Dublin, **2**: (In press).

WILLIAMS, E. G., and STEWART, A. B. 1943. Studies of phosphate fixation in Scottish soils. 1. The recovery of added phosphate from a soil of the acid igneous group. *J. Agr. Sci.* **33**: 179–189.

WILLIAMS, E. G., and REITH, J. W. S. 1948. The relative effectiveness of phosphatic fertilizers. *Empire J. Exptl. Agr.* **16**: 1–13.

WILLIAMS, E. G., REITH, J. W. S., and INKSON, R. H. E. 1952. Readily soluble phosphorus values and crop responses for different soils. *Trans. Intern. Soc. Soil Sci.*, Joint Meeting of Comm. II and IV, Dublin, **2**: (In press).

CHAPTER XV

World Phosphorus Fertilizer Production, Consumption, and Potential Needs

V. IGNATIEFF and G. J. CALLISTER

I. Introduction

In a recent study of the nutritional status of sixty-four countries by the Food and Agriculture Organization of the United Nations (FAO) it was found that a major part of the world's population is undernourished. The survey revealed that nearly 60 per cent of the people live in countries where average food supplies are less than 2250 calories per day. Because of the rapidly growing population of these countries, the food supplies available per person today are less than they were before World War II. The pressing need, therefore, confronting agriculture in the greater part of the world is for increased food production.

Some food consumption goals which are considered as possibly attainable by the end of this decade have been calculated by FAO. Although these target figures take into account sound nutritional principles for the world's population, they are not based upon optimum standards for most countries. Rather, they represent improvements in the quality and quantity of the national diet that could be and should be achieved. The gross world supplies needed to meet these goals are the following increases above current levels expressed in per cent in rounded-off figures:

a. Cereals, 20 per cent.
b. Starchy roots, 13 per cent.
c. Pulses, 60 per cent.
d. Sugar, 12 per cent.
e. Meat, eggs, and milk, about 40 per cent.

Achievement of these targets will require both extension of the total area under crops and the improvement of unit productivity of both crop and livestock production.

In implementing such expanded production programs, many vital and difficult factors are involved. Among them, and of increasing world importance, are the provision of more adequate plant nutrient supplies

from all available sources—farm-produced, natural organic, and chemical sources—and the more efficient use of plant nutrients. Especially is this vitally necessary in the many food-deficient areas.

A very important factor necessary to a higher agricultural production in countries all over the world is a more adequate supply and use of phosphorus. It is, therefore, well to examine the world production and consumption of commercial phosphorus fertilizers.

The level of consumption of phosphorus in any country, as of fertilizers supplying other plant nutrients, depends on several factors. Among them are:

a. Soil type.
b. Climate.
c. Crops.
d. Type of farming.
e. Density of population.
f. State of industrialization of the area.
g. Technical enlightenment of the farmers.
h. Economic conditions.

In appraising potential world phosphorus needs one is immediately confronted with these factors. Even if only climate, crops, and types of farming were considered, they alone present enough problems to make an assessment of world phosphorus needs a difficult undertaking. Because crops differ in their requirements for phosphorus and in their ability to extract this nutrient element from the soil, what may be an adequate supply for one crop may be inadequate for another. Again, crops grown on the same soil types under different systems of farming may require different fertilizer treatment. Intensity of farming will also have a marked effect on fertilizer requirements.

Notwithstanding the difficulties and limitations imposed by existing world conditions, it is realized that at least a preliminary review of potential phosphorus needs, based on food supply and agronomic considerations, might well be made. Such appraisals would assist in future planning and would be of special value in formulating policies for increasing food production, particularly in deficit areas. It is hoped that this preliminary statement may be followed by more detailed studies by interested groups. It is emphasized also that in no sense is this review a forecast of actual phosphorus consumption. Such a study, which would have to take into account economic factors, is outside the scope of this paper. The considerations here are solely the need for more ample food supplies and the agronomic factors affecting phosphorus needs.

In making an assessment of world phosphorus needs, it is assumed also that the other requirements affecting crop production are satisfied,

including the use of nitrogen, potassium, and such other elements as may be necessary. It would be unfortunate if an impression were created that the increased use of one plant nutrient element, phosphorus, would in itself greatly alleviate the world food shortage.

II. Phosphorus Fertilizer Production and Consumption: Prewar and Postwar Years (1936–1938 and 1946–1947; 1948–1949 and 1950–1951)

1. Characteristics of Prewar Years

From the figures for the world production and consumption of phosphates by continents and countries given later in Tables I and II (Food and Agriculture Organization of the United Nations, 1946, 1947), it will be noted that the chief characteristics of prewar production and consumption were briefly: Europe produced approximately 60 per cent and consumed well over one-half of the world phosphorus fertilizer production, North and Central America produced 19.2 per cent, Oceania 9.3 per cent, Asia 7.3 per cent, and Africa and South America the small balance of 2.7 per cent. Japan was by far the largest producing country in Asia.

Thus, before the war there were three highly industrialized regions in the world that produced and consumed phosphorus fertilizers: (a) Western Europe, (b) Eastern United States, and (c) Japan. These three areas had these factors in common:

1. A relatively high density of population.
2. Intensive farming practices (although the degree varied with different countries).
3. Considerable use of commercial fertilizers producing good crop responses on soils which are not naturally very fertile, but have a reasonably adequate supply of water.

High density of population and insufficient crop production, however, have not always resulted in the use of larger quantities of commercial fertilizers. India and China, each with a population of over four hundred million people, scarcely used any. The same is true of territories in Southeast Asia.

In all these areas the absence of industrial developments meant the minimum development of fertilizer industries, and therefore fertilizers could only have been obtained from overseas. Because of high transportation charges and other factors, the cost to the farmer was often high. Elsewhere in the world there were other reasons for the low consumption of fertilizers. Large tracts in the U.S.S.R., Africa, and South America remained so sparsely populated that it had not been necessary to cultivate the land intensively. In some areas, such as in the Middle East, lack of water was a limiting factor.

2. *World Production of Phosphorus Fertilizers*

During World War II, many countries in Europe, Asia, and Oceania were cut off from normal sources of fertilizer supply, both of raw materials and finished fertilizers. Many plants suffered war damage. Overall phosphorus fertilizer production and consumption in Western Europe, with the exception of the United Kingdom, declined. The production of basic slag, an important source of phosphorus in Europe, also declined.

The facilities for producing phosphate rock on some of the islands of the Pacific, particularly Ocean Island and Nauru, were destroyed, and this severely affected the supply of phosphate rock to Australia and New Zealand. As in Europe, superphosphate plants in China (Taiwan) and Japan suffered war damage. Production in Asia and Oceania declined. Critical war shortages occurred.

The most significant development of this period was the greatly increased production in North America, both of rock phosphate and phosphorus fertilizers, from 677 thousand tons P_2O_5 (all phosphorus fertilizer) per annum in the immediate pre-war years to 2180 thousand tons P_2O_5 in 1950–1951. This is the most significant increase in any continent during the war period. In the United States, the largest producing country, the increase was chiefly in the form of superphosphate, normal grade, and triple superphosphate; in Canada, in the forms of ammonium phosphates—11–48–0 and ammonium phosphate-sulfate—16–20–0. This growth in production enabled North America to assist other countries in need during the period of critical shortages.

Phosphorus fertilizer production in Europe again reached prewar level in 1947–1948 and increased by 28.5 per cent above this level by 1950–1951. Recovery in Asia was slower. It was not until 1950–1951 that prewar status was again reached. In Africa, Oceania, and South America production in 1950–1951 was much higher than in an average prewar year (Food and Agriculture Organization of the United Nations: 1946, 1947, 1949, 1950a, 1951c, 1952).

Four areas supply most of the phosphate rock used in the manufacture of chemical phosphorus fertilizers. They are the United States, North Africa, the Islands of the Pacific and Indian Oceans, and the U.S.S.R. This is due to the fact that the most efficient processes now in customary use for the manufacture of phosphorus fertilizers requires that the phosphate rock be of the highest grade possible, i.e., 30 per cent P_2O_5 or more. Although mineral phosphates are widely scattered throughout the world, ores of the above grade in sufficient volume have been found in comparatively few places. Table II indicates the major

TABLE I

TOTAL PHOSPHORIC ACID (P_2O_5) SUPPLIED BY SUPERPHOSPHATE, BASIC SLAG, AND OTHER FORMS OF PHOSPHATE[a,b]

(PRODUCTION PREWAR AND FOR YEARS ENDING JUNE 30, 1947, 1949, AND 1951)

Country	*Prewar*[c]	*1946–1947*	*1948–1949*	*1950–1951*
		(Thousand metric tons)		
Europe				
Belgium and Luxembourg	256.6	181.9	357.2	352.1
Czechoslovakia	50.9	44.9	55.3	56.0
Denmark	64.1	61.2	75.3	73.8
Finland	11.7	15.9	34.5	49.0
France	406.0	294.0	426.9	479.5
Germany	474.7	128.2	323.4	399.7
Federal Republic		(92.2)	(280.4)	(373.7)
Soviet Zone		(36.0)	(43.0)	(26.0)
Greece	10.3	11.9	14.5	40.0
Hungary	8.2	0.0	4.0	4.0
Ireland	22.1	18.6	24.0	30.0
Italy	232.9	157.7	251.2	310.0
Netherlands	100.1	100.1	163.2	166.3
Norway	4.9	9.5	10.9	19.0
Poland	22.9	30.0	50.0	50.0
Portugal	32.1	50.8	41.0	71.5
Spain	163.5	136.0	120.0	140.0
Sweden	45.3	69.5	80.9	98.6
Switzerland	3.3	9.7	9.1	31.0
United Kingdom	121.6	280.2	328.0	278.3
Yugoslavia	3.9	2.0	2.0	6.3
Other countries	30.9			
Total	2066.0	1602.1	2371.4	2655.1
North and Central America				
Canada	12.9	115.2	109.6	105.0
Mexico		3.6	4.0	7.9
United States	664.1	1630.9	1870.0	2067.0
Other countries			5.1	.1
Total	677.0	1749.7	1988.7	2180.0
South America				
Argentina		5.0	5.0	9.0
Brazil		12.4	5.0	13.5
Chile	6.5	7.4	14.3	15.0
Peru	17.7	16.0	16.8	24.0
Other countries		2.8	0.8	.6
Total	24.2	43.6	41.9	62.1

TABLE I (*Continued*)

Country	Prewar	1946–1947	1948–1949	1950–1951
		(*Thousand metric tons*)		
Asia				
India	0.8	1.7	5.1	14.0
Israel		1.4		8
Japan and Ryukyus	246.6	70.8	166.5	231.7
Taiwan	3.7		3.1	8.7
Turkey		0.7	1.1	2.6
Thailand			1.0	1
Total	251.1	75.0	176.9	257.9
Africa				
Egypt	9.0	2.7	7.5	12.7
French North Africa	21.2	32.0	36.0	[d]
Union of South Africa	24.4	48.0	65.0	115.0
Other countries	5.5			9.2
Total	60.1	82.7	108.5	136.9
Oceania				
Australia	248.4	245.4	318.0	345.9
New Zealand	89.5	118.0	124.7	133.8
Total	337.9	363.4	442.7	479.7
WORLD TOTAL	3416.3	3916.5	5130.1	5771.7

[a] Food and Agriculture Organization of the United Nations (1946, 1947, 1949, 1950, 1951c, 1952).

[b] Data are exclusive of the U.S.S.R. and a few countries with small production, for which figures are incomplete. Exclusive of phosphate rock.

[c] Prewar figures are two- or three-year averages within the period 1935–1939.

[d] Now included with France.

TABLE II

PHOSPHATE ROCK PRODUCTION BY IMPORTANT PRODUCING AREAS[a]

Producing Area	1938	1946–1947	1948–1949	1950–1951
		(*Thousand metric tons rock*)		
United States of America	3,922	9,145	9,246	10,711
North Africa	4,106	5,204	5,856	7,000
Ocean Island and Nauru	1,159	238	780	1,200
U.S.S.R.	2,363	1,600	2,200	?

[a] Food and Agriculture Organization of the United Nations (1946, 1947, 1949, 1950, 1951c, 1952).

world phosphate rock production in recent years in comparison to prewar years.

3. *World Consumption of Phosphorus Fertilizer*

In 1950–1951 world consumption of phosphorus fertilizer reached the record level of 5.7 million tons P_2O_5. By 1950–1951 (see Table III),

TABLE III

CONSUMPTION OF PHOSPHORIC ACID (P_2O_5) (EXCLUDING GROUND ROCK PHOSPHATE)[a]

Country	Prewar[b]	1946–1947	1948–1949	1950–1951
	(Thousand metric tons)			
Europe				
Austria	12.8	7.0	25.6	40.0
Belgium and Luxembourg	85.6	84.4	95.9	84.2
Czechoslovakia	47.9	44.9	60.0	60.0
Denmark	67.3	52.8	71.7	84.5
Finland	28.7	32.5	67.7	61.2
France	406.0	289.0	348.8	412.0
Germany	564.2	186.0	460.9	477.4
Federal Republic		(136.0)	(390.9)	(411.4)
Soviet Zone		(50.0)	(70.0)	(66.0)
Greece	7.4	11.9	14.5	19.0
Hungary	10.4	0.0	8.0	11.0
Iceland		0.6	1.0	1.0
Ireland	26.7	24.0	41.3	50.3
Italy	261.9	146.6	219.6	303.0
Netherlands	100.1	119.5	122.0	120.0
Norway	15.3	26.5	32.3	84.0
Poland	32.9	35.0	50.0	60.0
Portugal and DOT's[c]	32.9	51.1	41.0	57.0
Spain	165.6	102.0	120.0	136.0
Sweden	50.9	67.0	80.9	105.0
Switzerland	24.2	31.4	30.0	33.0
United Kingdom	180.5	297.6	379.2	380.0
Yugoslavia	4.4	2.0	3.0	6.3
Total	2125.7	1611.8	2273.4	2534.8
North and Central America				
Canada	34.0	85.3	101.6	105.3
Cuba		7.7	11.0	19.3
Mexico		3.6	7.2	7.5
United States	671.9	1575.0	1770.0	2028.0
Other Central American Republics	5.0	1.7	2.7	2.1
Total	710.9	1673.3	1892.5	2162.2
South America				
Argentina		6.1	6.5	7.0
Brazil		21.0	22.0	33.0
Chile	5.9	26.5	22.6	11.8
Colombia		1.6	1.6	5.0
Ecuador			0.6	.1
Peru	16.4	16.0	16.8	24.0
Uruguay		2.8	1.5	1.5
Other countries	1.8		0.5	.2
Total	24.1	74.0	72.1	82.6

TABLE III (*Continued*)

Country	*Prewar*[b]	*1946–1947*	*1948–1949*	*1950–1951*
		(*Thousand metric tons*)		
Asia				
Burma			0.1	0.1
Ceylon	9.1	1.1	2.7	2.0
China	0.5	10.4		
Cyprus	0.6			3.3
India	1.6	5.0	5.1	14.0
Indonesia	0.8	0.6	2.1	11.0
Israel			2.5	6.5
Japan and Ryukyus	239.9	71.0	165.0	237.6
Korea[d]	21.0	40.0	50.0	1.2
Lebanon			0.5	0.7
Taiwan	13.9		8.5	14.9
Turkey	0.0	0.8	0.8	2.5
Other countries	22.3	3.4	3.5	2.4
Total	302.7	132.3	240.8	295.2
Africa				
Egypt	9.0	6.5	13.5	21.8
French North Africa	24.9	30.1	36.0	[e]
Union of South Africa	42.0	52.0	60.5	108.0
Other countries	4.1		2.4	18.9
Total	80.0	88.6	112.4	148.7
Oceania				
Australia	247.8	245.4	318.0	345.9
New Zealand	101.9	118.0	141.0	143.5
Other countries				.2
Total	349.7	363.4	459.0	489.6
WORLD TOTAL	3593.1	3943.4	5050.7	5708.3

[a] Data are exclusive of the U.S.S.R. and a few countries with small consumption for which figures are incomplete. (Food and Agriculture Organization of the United Nations, 1946, 1947, 1949, 1950, 1951c, 1952).

[b] Prewar figures are two- or three-year averages within the period 1935–1939.

[c] DOT's refers to "Dependent Overseas Territories."

[d] The figures for Korea represent consumption for the whole country before the World War II and only for South Korea after the War.

[e] Now included with France.

consumption in each continent except Asia had exceeded that of prewar years. Consumption in Europe was 19.2 per cent higher, but had declined from 59 per cent of the prewar world total to 44 per cent in 1950–1951. Consumption in North and Central America increased by 203 per cent during the same period and amounts to about 38 per cent of the world total. Consumption in Oceania, about 9 per cent of the total, increased 40 per cent during this period, while in South America it was trebled and in Africa consumption increased by 80 per cent above

1936–1938 levels. In Asia consumption was less than half prewar in 1946–1947 and slightly below in 1950–1951 (Food and Agriculture Organization of the United Nations, 1946, 1947, 1949, 1950a, 1951c, 1952).

By 1950–1951 the significant and vital world development was the ever-increasing number of countries that used phosphorus fertilizers. In strong contrast to the prewar situation, in addition to the industrial areas, many other countries in the more distant places of the world had increases in phosphorus consumption, including Ceylon, India, Cyprus, Indonesia, Israel, Malaya, Egypt, Mauritius, Rhodesia (N), Tunisia, and many others.

Thus the problems of an adequate phosphorus supply to meet an increasing world demand are among the more important problems in the field of commodities today. The immediate outlook and current problems are discussed in the following paragraphs.

4. Immediate Outlook and Problems of Supply

Changes of a vital character in the production and distribution of phosphorus fertilizer are now culminating in developments influencing production and supply throughout the world. Briefly stated, these developments are threefold:

1. A very rapid increase in world production has taken place. In 1946–1947, the total world production of P_2O_5 was 3,916,500 metric tons (exclusive of the U.S.S.R.). In 1950–1951, world production reached 5,770,000 tons, with a phenomenal increase of 1,853,500 tons in a period of four years (Food and Agriculture Organization of the United Nations, 1950a, 1951c, 1952).

2. Plant capacity for the production of concentrated phosphorus fertilizer materials, i.e., with a higher P_2O_5 content than 16 to 22 per cent, has increased. Within the overall gain of 1,853,500 tons P_2O_5 the volume of concentrated phosphorus fertilizer—as triple superphosphate, ammonium phosphate, nitric phosphate, calcium metaphosphate, defluorinated phosphate rock, and other types—has increased, and plans are being made to produce larger tonnages at an early date (Food and Agriculture Organization of the United Nations, 1951c).

3. A world shortage of native or elemental sulfur has developed (Food and Agriculture Organization of the United Nations, 1951c). By far the major part of the world production of phosphorus fertilizers requires sulfur for making the sulfuric acid necessary in the manufacture of superphosphate (16–22 per cent P_2O_5), the most widely used and most important carrier of phosphoric acid. The world production of sulfur in forms that can be used in present plant installations has not been

able to keep pace with the demand. It is estimated that the demand for elemental sulfur, to which much of the world production of sulfuric acid is now geared, is presently at the rate of one million tons above the visible supply. This shortage is particularly acute in some food-exporting countries.

The problems of maintaining an adequate phosphorus fertilizer supply facing the world today may be briefly stated as follows:

1. The development of new sources of sulfur from pyrites, from the catalytic cracking plants in new oil refineries, from anhydrite, natural gas, smelter gases, and from other industrial sources.

2. The manufacture of phosphorus fertilizers requiring a minimum of sulfur or none, such as the acidulation of phosphate rock with nitric acid and the defluorination of phosphate rock.

3. The utilization of indigenous raw materials that are not normally used in the manufacture of phosphorus fertilizers. One instance is the manufacture of fused phosphate called "soda phosphate" in Kenya. This material is made from Uganda phosphate (apatite), using only soda ash at a low temperature of 900° C. Another is the manufacture of serpentine fused phosphate in Taiwan. It has been found that these citrate-soluble phosphates can be effectively used in the regional agriculture where these fertilizers are produced.

4. Surveys for new sources, particularly for high-grade phosphate rock and sulfur, in the industrially less developed regions.

Thus, although the potential needs for phosphorus fertilizer are much higher than current consumption, the solution of supply problems, especially in many of the industrially less-developed regions of the world, goes hand in hand with increasing utilization.

III. Potential Phosphorus Fertilizer Needs

How shall the potential phosphorus fertilizer needs of the world be appraised, and in what form shall the needs be expressed? The appraisal of need as used here is based chiefly on two factors:

1. The response of crops to the use of phosphorus as determined by field experimentation. Fertilizer requirements largely depend on differences in soils. For example, nitrogen, and possibly other elements, are needed for wheat in Europe, but in Australia the need is principally for phosphorus, which is the chief fertilizer used. In discussing potential needs, therefore, our present knowledge of the broadly defined soil areas of the world, especially in relation to phosphorus supply or requirements, will be considered. After this introductory statement, further details of the more important soil groups and their relation to phosphorus needs are given wherever possible by continents.

2. The regional consumption of phosphorus. It is appreciated that the current volume of consumption is determined possibly as much by general economic activity as by agronomic factors and is thus in itself not a true basis of actual need. The present status of utilization gives some indication of need, however, and is taken into account as a convenient starting point in appraising future need.

1. Phosphorus Requirements in Relation to Soil Regions

From a world point of view (see Fig. 1) there are six major soil regions, some of which require more phosphorus than others (Kellogg and Orvedal, 1950). The major soil regions are:

(a) Black, Brown, and Dark Gray Soils of Temperate and Tropical Grasslands.

(b) Light Gray and Red Soils of Deserts.

(c) Gray and Brown Soils of the Temperate Forests.

(d) Red Soils of Warm and Tropical Forests and Savannahs.

(e) Organic Soils.

(f) Alluvial Soils.

a. Black, Brown, and Dark Gray Soils of the Temperate and Tropical Grasslands. Prairie soils are normally high in fertility but may respond well to phosphorus. Degraded Chernozems are medium in natural fertility; they respond well to phosphorus as well as to nitrogen and potassium. The Chernozems and Reddish-Chestnut soils are, in general, high in fertility and productivity, but may respond to phosphorus fertilizer. These major soil groups occur in the temperate zones of Europe, North America, and Asia, and on them much of the world's crops are produced.

The dark gray and black soils of tropical savannahs are of medium productivity without irrigation; of high fertility with irrigation. These soils require nitrogen, but some crops also give good response to phosphorus. The Chestnut, Brown, and Reddish-Brown soils, when irrigated, respond to phosphorus as well as to nitrogen.

b. Desert Soils. When irrigated, desert soils are generally well supplied with all the plant nutrients, except nitrogen, because little organic matter, and consequently little nitrogen, has accumulated in the soil. After the need for nitrogen has been met, phosphorus may be needed in some places, and also some of the other elements like iron and zinc.

c. Gray and Brown Soils of the Temperate Forests. These soils are also important in major crop-producing regions. They are generally, but not always, acid. Liming is usually the first requirement. Next to lime, nitrogen is most commonly needed, followed by phosphorus and

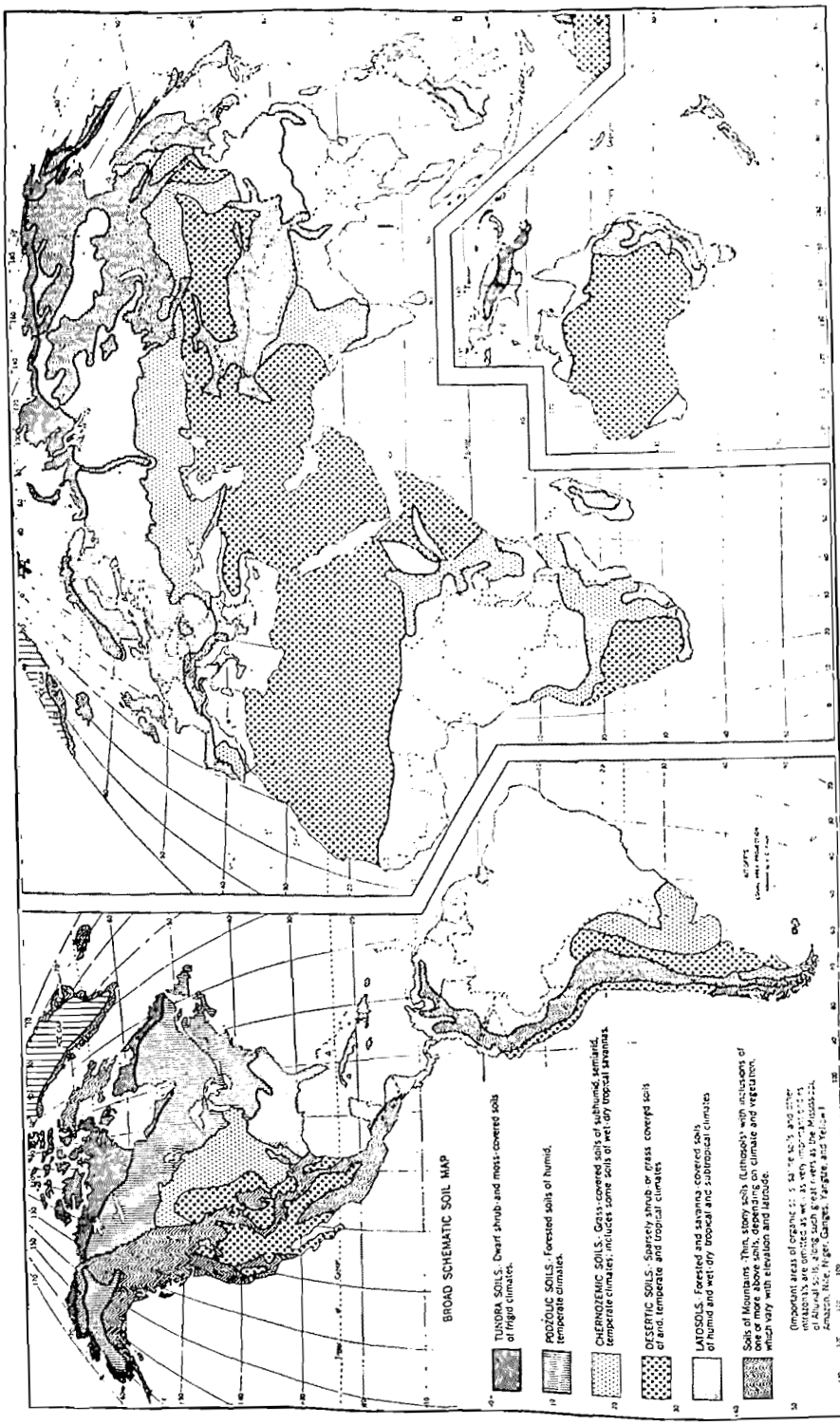


FIG. 1. Schematic soil map of the world showing soil zones.

potassium. In many places, particularly on sandy soils, some of the other elements such as boron, manganese, zinc, calcium, magnesium, or iron may be deficient. Nitrogen can be maintained wholly or partly through the growth of legumes and the use of animal manures.

Podzols with much Bog, Gray-Brown Podzolic, and Brown Forest soils are the major soil groups of the temperate forest region. The Brown Forest soils are naturally the most productive, whereas the Podzols are the least productive in their native state. Many Podzols, however, have been brought to a high state of productivity through good husbandry. In general, they are deficient in nitrogen and phosphorus, with potassium required in many instances.

d. Red Soils of Warm and Tropical Forests and Savannahs. These groups have had few soil surveys. The more important soil groups of these tropical forests and savannahs are: Latosols (red lateritic, reddish-brown lateritic, etc.), Red-Yellow Podzolic soils, and Terra Rosa soils. However, other soils occur mixed with them, such as highly productive young soils from recent volcanic deposits and old, relatively infertile soils of the undulating plains. For these reasons, there are many important subdivisions. These soils are usually more thoroughly leached than the soils of the temperate zone forests and have less capacity to prolong the good effects of fertilization. Although plants grow quickly, organic matter is rapidly lost. Its maintenance is an important problem. Phosphorus quickly tends to become fixed in the non-organic part of the soil and is less available to plants. The great need for phosphorus fertilizers to help establish leguminous cover crops in the humid tropical regions, especially on acid soils, is stressed by a number of authorities.

e. Organic Soils. These occur in many small areas in Podzol, Gray-Brown Podzolic, and Brown Forest soil areas. Locally they may be of great relative importance. They are nearly always deficient in potassium and phosphorus, especially the former, and also very frequently in other nutrient elements. These soils vary widely in acidity and, although the nitrogen content of organic soils is high, the nitrogen is not always in readily available form in sufficient quantities for the best growth of some plants.

f. Alluvial Soils. Generally more fertile than upland soils of the watershed, Alluvial soils usually have less of the nutrient deficiencies common in the regions from which the sediments are derived. For instance, although phosphorus deficiency is acute in the residual soils of the Union of South Africa, the Alluvial soils have such an ample supply of available phosphorus that even after twenty to thirty years of intensive cropping, for example, to alfalfa, phosphorus fertilizers are not yet used.

The major subdivisions are the Alluvial soils of a forest watershed, Alluvial soils of grassland watersheds, and Alluvial soils of the humid tropics. The first group is likely to need lime in addition to nitrogen, phosphorus, and potassium unless derived from limestone. Some of the secondary elements may also be needed. Alluvial soil from grassland watershed is usually more fertile, but in many places crops respond to phosphorus and nitrogen. The soils of the humid tropics are likely to need both phosphorus and nitrogen. In some cases, rock phosphate has proved to be as effective as superphosphate.

2. *Evaluation of Phosphorus Fertilizer Needs by Continents and Countries*

The phosphorus needs of the soil groups are discussed in more detail in the sections that follow on Asia, Africa, Latin America, Oceania, Europe, and North America. Tonnages are used as the most convenient measure of relative emphasis that can be quickly understood. The tonnages given here should not be regarded strictly in their numerical sense but rather as typifying a broad measure of need above the amount being currently used. Such tonnages are not directly related to possible future demand or to actual future consumption.

a. Asia. This continent, with some of the most densely populated areas of the world, consumes relatively small quantities of plant nutrients as commercial fertilizers—295,200 tons P_2O_5 out of a world production of 5,770,000 tons in 1950–1951. The use of plant nutrients should be greatly increased to assist in raising the level of agricultural production, especially of food crops. With the notable exception of Japan, and to some extent of South Korea and China, crop yields in the area as a whole, as shown in Table IV, are relatively low. It is evident that crop yields can in many cases be increased by the use of phosphorus.

A basic problem, however, in increasing the consumption of commercial fertilizers is the assurance of an adequate water supply, either by rainfall or irrigation. In Japan, Korea, and Taiwan (Formosa) fertilizers are used on food crops such as rice, but in Asia as a whole they are more often used with cash crops such as tea, sugar cane, etc. For the attainment of better nutrition levels, it is the increases in production of cereals, particularly rice, and of the pulses that are commonly grown in rotation with rice and vegetables, that have to be secured. More attention should be directed to the possibilities of using commercial fertilizers in greater quantities and on wider areas with these particular crops.

Paddy rice (grown in water) is a crop which has received the great-

TABLE IV

FOOD CROP YIELDS IN SOME ASIAN COUNTRIES (1948)[a]

Country	Rice	Wheat	Sorghum	Millet	Maize
	(100 kg./hectare)				
Burma	13.6	8.2	...	....	5.8
Ceylon	6.6	....	....	....	5.3
China	25.1	11.2	12.9	14.9	15.0
India	11.7	6.6	2.8	3.7	5.9
Indonesia	15.5	....	.	....	...
Japan	37.2	15.8	14.0	10.8	13.4
Pakistan	13.7	8.2	4.3		10.7
Philippines	11.5	....	....	....	7.9
South Korea	27.9	7.3	8.1	6.8	5.0
Thailand	12.6	...	....	...	7.1

[a] Food and Agriculture Organization of the United Nations (1950b).

est attention in fertilizer trials in Asia, and considerable data have been accumulated for this crop. With pulses and vegetables, the main guide is a body of practical experience and simple experiments. There is real evidence that the yields of pulses and leguminous forage crops can be substantially increased by the use of phosphates.

The major results of experimental work in several Asian countries can be summarized briefly as follows:

On soils of *Lower* and *Upper Burma* (Ignatieff, 1951, p. 19) phosphorus fertilizer applied alone gave increases in yield of paddy of 15 per cent in the year of application, followed by similar increases for two to four years owing to residual effects.

Taken as a whole, *Ceylon* soils other than those derived from limestone (Ignatieff, 1951, p. 23) are poor in organic matter and in available lime and phosphorus, but fair in nitrogen and potassium. Experiments with paddy rice have been conducted at more than ten experiment stations on different soil types. The general finding has been that phosphorus and nitrogen are the plant nutrient elements most deficient in Ceylon paddy soils. Ammonium phosphate applied at the rate of 125 kg. per hectare has given over a period of years an average increase in yield of 543 kg. per hectare (29 per cent) at several experiment stations. Bonemeal applied at the same rate induced a response of 156 kg. per hectare (8 per cent).

In Ceylon up to the present, phosphorus fertilizers have been used chiefly on tea (average application, 28 kg. P_2O_5 per hectare) and to a limited extent on rubber and coconut trees. Very little has been used on paddy.

In *China* (Yao, 1948, p. 20) it has been estimated that 75 per cent of cropped land will respond to an application of nitrogen, 40 per cent to phosphorus, and 14 per cent to potassium. Deficiencies in soil phosphorus have been reported by Yao (1948), particularly on the calcareous alluvium (Huai River Valley), Podzols, Shantung Brown soils, yellow earths (high, alluvial, and paddy lands), noncalcareous alluviums (Chengtu and Yangtze river valleys), and red earths (high, alluvial, and paddy lands). Results of experiments conducted in seventeen provinces of China over a period of years have shown that with applications of 60 kg. P_2O_5 per hectare average increases of 625 kg. of rice, 446 kg. of rapeseed, and 397 kg. of wheat per hectare were obtained (Yao, 1948, p. 32).

In the island of *Taiwan* (Formosa) commercial fertilizers are used more intensively than on the mainland of China. Nitrogen is the chief fertilizer; phosphorus fertilizers are also used, however, and currently indigenous production is being increased to meet the demand. Potassium is also required in some instances. The western side of the island is intensively cultivated. Fertilizers are chiefly used on rice and sugar and to some extent on other crops.

In *India* the paddy crop has been most widely used in fertilizer experimentation and it has been shown that for all major soil groups—Latosols (red loams, red sandy soils, laterite, and lateritic soils), black cotton soils, and even the alluvial soils, which are typical paddy soils—the prime requirement for paddy is nitrogen (Stewart, 1947, p. 148; Ignatieff, 1951, p. 34).

With phosphorus the results have been less positive, but indications are that phosphorus increases paddy yields in certain soil types if the nitrogen requirement of the crop has been met. The recommendation in the majority of the important rice-growing states is for the use of phosphorus on rice at the rate of 15 to 30 kg. P_2O_5 per hectare. Widely conducted field experiments at Himayatsagar (Hyderabad), Nagina and Gorakhpur (Uttar Pradesh), Maruteru, Coimbatore and Aduturai (Madras State), in general, support this recommendation.

Somewhat similar results (Stewart, 1947, p. 117) have been obtained with millets, oil seeds, and pulses, although relatively fewer trials have been conducted with these crops.

Peanuts, usually unirrigated, are grown on the Indian Peninsula. This crop uniformly showed response to superphosphate (Stewart, 1947, p. 144) applied at the rate of 35 to 45 kg. P_2O_5 per hectare in trials at Akola and Buldana in Madhya Pradesh and in the Deccan Canals tract in Bombay. The average increase from 16 trials was 8.4 kg. per

kilogram P_2O_5 applied. Response to phosphorus alone was not observed in Tindivanam in Madras, but the response to combinations of nitrogen and phosphorus was considerable.

The consensus is, therefore, that with the larger and wider use of nitrogen fertilizers, the need for phosphorus will become even more evident, not only for rice but for other crops.

In *Indonesia* (Ignatieff, 1951, p. 46) soils deficient in phosphorus are quite common in the rice-growing areas of Java, especially in the extensive lowland plains where nearly all arable land is occupied by paddy. These soils probably occur over large areas on the other islands of Indonesia, but no exact data on their distribution are yet available. The soils deficient in phosphorus in Java include:

1. The white dacite bleached tuff and the yellow old dacite tuff Laterite of Northern Bantam and West Batavia.

2. The yellow and grayish yellow laterite soils in Krawang and Indramaju.

3. The various types of marly soils found over wide areas from Tjiandjur in West Java to Pasuruan in East Java and island of Madura.

4. The sandy quartzitic soils in East Java and Madura.

Results at eight experimental stations have shown that applications of phosphorus fertilizers at the rate of 45 kg. per hectare increased yields from 0.6 to 1.3 tons of stalk paddy per hectare.

In *Pakistan* (Ignatieff, 1951, p. 53) except for the soils of Himalayan and submountaneous tracts, the cultivated soils are formed mainly from alluviums, part of which are covered by aeolian deposits in the Punjab.

In *West Pakistan* the soils generally have an alkaline reaction and accumulations of salts are common both in Punjab and Sind. These soils are low in nitrogen and organic matter but fairly well supplied with phosphorus and potassium. In trials on unirrigated wheat (Stewart, 1947, pp. 130–135) at a number of experiment stations over a period of years, it has been found that responses to phosphorus alone were good, with increases of 7 kg. of wheat per kilogram of P_2O_5 being obtained from applications of 37 kg. P_2O_5 per hectare.

In irrigated trials on wheat there is a consistent response to nitrogen, to phosphorus, and to the combination of these two plant nutrients. Not many trials have been conducted with phosphorus alone, but indications are that increases in yield from 7 to 29 kg. per kilogram of P_2O_5 applied can be secured when superphosphate is applied at the rate of about 20 kg. of P_2O_5 per hectare.

In *East Pakistan* much of the recent Alluvial soil contains fair

quantities of lime, phosphorus, and potash. The red soils derived from old alluvium, however, are acutely deficient in phosphorus as well as in nitrogen and lime.

In the *Philippines* a large proportion of the soils (Ignatieff, 1951. p. 71) are Latosols (the red loams, red lateritic, reddish-brown lateritic) and Red-Yellow Podzolic soils. These soils have developed from a variety of parent materials, including volcanic tuff, basalt, andesite. rhyolite, dacite, limestone, shale, sandstone, and slate. Many of the soil types appear to be deficient in nitrogen and phosphorus, and some crops, especially vegetables, may also benefit by the application of potassium fertilizer on some soil types. There are also important areas of Alluvial soils, which have the widest distribution and are of the greatest agricultural importance in the great central plain of Luzon. Chemical analysis indicates that most soils of this plain are probably deficient in phosphorus and potassium.

Experiments conducted in various parts of the Philippines have shown that substantial increases in yield of paddy are obtained by the use of phosphorus alone and that still larger increases are obtained by the use of phosphorus in combination with nitrogen, and on some soil types with potassium as well. For instance, at the College of Agriculture, Laguna Province, the results of several years of experimentation show that superphosphate applied at the rate of 35 kg. P_2O_5 per hectare gives an average increase of about 500 kg. of paddy. At the Albang Rice Experiment Station in Rizal, increases of 250 kg. per hectare were secured by the use of 10 kg. P_2O_5.

Up to the last year or two, most of the fertilizer used in the Philippines has been applied to sugar cane. Experimental results in Negros Occidental, which is the chief sugar-growing province, have shown that yields of sugar can be doubled by the use of some 80 kg. of nitrogen per hectare. On some of the upland soils, however, the best results are not obtained unless some phosphorus is included.

Agriculturally, *Thailand* (Ignatieff, 1951, p. 71) can be divided into five regions—the Bangkok Plain, Northern, Northeastern, Southeastern, and Peninsular. The soils of the Bangkok Plain, which is the chief paddy-growing region, are predominantly heavy dark clays developed from fine-grained alluvium. The soils of the valleys of the Northern Region, which is mostly rough mountainous land, are fairly fertile. On the other hand, the soils of the upland Northeastern Region, which has an undulating landscape, are very poor. The mountainous Southeastern Region and the Peninsular are not very important agriculturally, but it is suspected that some of the soil types in this region are phosphorus-deficient.

Preliminary fertilizer experiments on the soils of the Bangkok Plain give indication of the need for phosphorus for paddy. Also, the practical experience of the cultivators in this region shows that better results are obtained with vegetables when phosphorus is applied, and bat guano has been used on vegetables here for a considerable number of years.

In *Viet-Nam* (Ignatieff, 1951, p. 82), in the Tonkin region, phosphate increased yields of paddy when applied alone or in combination with nitrogen. Best results were obtained on land to which manure was applied; on such land increases of 5.8 kg. of paddy per kilogram of P_2O_5 applied were obtained.

In *Japan*, using as a basis of comparison the five-year periods ending in 1882 and 1942, production per hectare of rice increased 70 per cent, wheat 140 per cent, common barley 119 per cent, naked barley 62 per cent, and tea 180 per cent.

In recent times the trend in soil fertility in Japan is upward because of the large amounts of commercial fertilizer, barnyard and green manures, composts, and night soil that have been applied. It is emphasized, however, that the higher yields attained in Japan have been secured not only by the efficient use of plant nutrients but also by the employment of many other improved practices affecting both the soil and the crop.

Many of the important agricultural soils (Swanson, 1946) are developed on volcanic ash. Ando soils, derived principally from volcanic ash materials, are found in all areas of Japan. Although they are dark-colored and friable, the organic matter in these soils has a higher C/N ratio and the soils are infertile in their natural state. The most important and most fertile soils, which support the bulk of the population, are the Alluvial soils developed in the lowlands. On these, paddy is grown in the summer; and in Southern Japan, these soils are also cropped to wheat and barley during the winter months.

The soils in Japan are not naturally fertile and for maximum crop production most require heavy fertilization and liming. The Ando soils, important upland soils, are especially low in available phosphorus. They are physically well suited to growing small grains, sweet potatoes, vegetables, mulberry, upland rice, pulses, tree fruits, tea, tobacco, and other dry-land crops. Responses to the application of phosphorus vary. On an average, the increase in the yield of paddy is only a few per cent (Working Party on Fertilizers, 1951, p. 51), except on some volcanic soils on which greater increases are obtained. Increases in yield of wheat and naked barley vary from zero to 55 per cent (Supreme Command for Allied Powers, 1947a). At the Saitama Prefectural Agriculture Experiment Station, dressings of 122 kg. of P_2O_5 per hectare in-

creased the yield of common barley from 495 kg. per hectare (control plot) to 4,233 kg., and dressings of 183 kg. P_2O_5 per hectare increased the yield of white potatoes from 9,163 kg. to 18,880 kg. per hectare.

The recommendations of the Ministry of Agriculture and Forestry for rates of application of phosphorus in the form of commercial fertilizer for some of the crops are given in Table V (Supreme Command for Allied Powers, 1947b, p. 51).

TABLE V

RECOMMENDED RATES OF PHOSPHORUS FERTILIZER APPLICATION IN JAPAN[a]

Crop	*P_2O_5 kg. per hectare* (*max.*)	(*min.*)
Paddy and upland rice	56	15
Wheat, barley	76	26
Sweet potatoes	62	30
White potatoes	72	38
Millet	53	37
Corn, peas	75	37
Beans	75	23
Tomatoes	85	64
Eggplant	101	42
Spinach	45	30
Carrots	36	15
Fruit trees	290	60

[a] Supreme Command for Allied Powers, Japan (1947b).

Asia at present is using 295,200 tons P_2O_5 annually, 237,600 tons in Japan, and 14,900 tons in Taiwan, leaving approximately 42,700 tons for all other consuming areas. Obviously this figure is far too low, but nonetheless it is difficult to suggest an adequate rate of phosphorus fertilizer consumption for this vast region. There is no question that crop yields must be increased to meet the demands of the growing population. Based on Japanese, and in part on Chinese and Korean experiences, it is equally clear that this can be done.

A reasonable approach is to consider the areas under rice, wheat, pulses, and oilseeds, which amount to about 175 million hectares out of a total of 329 million hectares, excluding Japan and South Korea. These crops have been selected not only because they are most important from the standpoint of human nutrition, but also they are the crops, particularly paddy, that are most likely to have an adequate supply of water. Furthermore, wheat, pulses, and oilseeds are usually grown on the more responsive soils. On the basis of one-sixth of the area receiving an annual dressing of 30 kg. P_2O_5 per hectare, which would

include vegetables and fruits, 900,000 tons of P_2O_5 would be required. This estimate of consumption is very conservative. There is sufficient evidence to indicate that at least the size of the area suggested would comprise soils responsive to phosphorus. Another 100,000 tons P_2O_5 should be allowed for industrial crops, such as sugar cane, tea, and cotton. For Japan and South Korea it is estimated that by 1960 400,000 tons per annum could be used. Were the fertilizers available, therefore, an annual consumption for Asia as a whole of 1.4 million tons P_2O_5 by 1960 would be a reasonable figure to suggest.

b. Africa. In Africa the results of field experiments in different countries indicate a definite need for phosphorus fertilizers on many soils and crops. This is confirmed by the fact that consumption has increased from 112,400 tons P_2O_5 in 1948–1949 to 143,700 tons in 1950–1951 and is still increasing. In a few countries fertilizer experiments have been conducted for a great number of years, and more recently this type of work has been undertaken in many more. The following summaries indicate the vital role of phosphorus in the agriculture of some of these countries in Africa, and the growing need in others.

In *Egypt* experiments by Gracie and Khalil (1948) show that average responses to ordinary superphosphate applied at the rate of 238 kg. per hectare were 1670 kg. per hectare dry weight of berseem (*Trifolium alexandrinum*), 240 kg. per hectare beans, and 380 kg. per hectare rice in husk. With twice that application, that is, with 476 kg. per hectare of superphosphate, average responses were 8 kg. per hectare of cotton lint, 104 kg. per hectare of wheat, 103 kg. per hectare of barley, and 80 kg. per hectare of corn. Thus, on the irrigated, permeable, somewhat salty, alluvial clay soils of the Nile delta notably good responses are given by beans and rice but only moderate responses by the four other crops. On the irrigated, feebly permeable, somewhat salty clay soils of the Gezira in the Anglo-Egyptian Sudan, cotton and sorghum have shown no response to applications of superphosphate. In these hot dry areas, water and nitrogen are the main needs.

Some outstanding increases in yield due to phosphorus fertilizers have been recorded in East Africa. Increments of 44 per cent in the yields of finger millet, corn, and soybeans have been obtained by the use of 125 kg. per hectare of ordinary superphosphate on red earths overlying concretionary ironstone in the Nyanza province of Kenya. Acid soils with a high degree of base saturation are not seriously phosphorus-deficient, however (Birch, 1951).

Hoyle (1951) and Hoyle *et al.* (1952) report that in *Nyasaland* corn and tobacco have responded strongly to nitrogen and less strongly to phosphorus, but have not responded to potassium. The quality of to-

bacco leaf was greatly improved by nitrogen and phosphorus fertilizers, whereas potassium seemed ineffective.

In *Northern Rhodesia* when rains are favorable, McEwan (1932) has noted that the fine-grained, moderately leached soils of the Upper Valley respond to applications of single superphosphate at the rate of about 100 kg. per hectare by increases in yield of corn grain of about 200 to 300 kg. per hectare. The residual effect of the application seems to be large.

In *Southern Rhodesia* good results have been obtained with the application of rock phosphate to the leguminous green manure crop preceding corn, whereas the application of phosphates on the corn crop itself is seldom economical (Rattray, 1951).

In *Nigeria* and the *Gold Coast*, fertilizer trials have been carried out not only at experiment stations but on peasant farms where lack of cultivation, wide sowing, and late planting are liable to cause low yields. The fragmented peasant farms of only a few acres are frequently so inaccessible by rail or road that the introduction of fertilizers has been considered impracticable.

The profitable use of phosphorus in the forest areas lying to the south of these countries may be dependent also on the use of nitrogen or potassium. However, there are large areas in which the use of superphosphate alone promises highly economic returns. These areas are roughly represented by that part of the Gold Coast lying north of latitude 10° N and that part of Nigeria lying between latitudes 10° and 13° N.

The Gold Coast area is of similar climate to that of N. Nigeria at the same latitude. The farming systems of the two areas are similar, with sorghum, millet, and peanuts as the main crops; in both areas the farmers are accustomed to apply organic manures to their homestead farms. Many of the soils are sandy, and derived from granite. Fertilizer responses in the two regions are strikingly similar. Greenwood (1951) and Nye (1952) have noted that in peasant hands an application of 67 kg. per hectare of ordinary superphosphate will produce an increase of 91 kg. of either grain or shelled peanuts in the year of application, and leave a residual effect not less than 50 per cent of the immediate effect. Significant residual effects have in fact been observed in Nigeria four years after the date of application.

Estimates of the areas which would derive immediate benefit from the use of superphosphate have been obtained from the acreage in peanuts which, grown in rotation with the two cereal crops, occupy between one-quarter and one-eighth of the arable land and indicate the area which could profitably be manured annually, assuming a residual

effect of two years' duration. They are: Nigeria, 647,488 hectares; Gold Coast. 20.230 hectares. If given the 62 kg. per hectare recommended for Nigeria. there is an immediate need for 36,000 tons of superphosphate per annum.

In an exploratory study of the soils of the *Belgian Congo* conducted by Kellogg and Davol (1949), the following major soil groups were recognized in the field: several groups of Latosols (Reddish Prairie soils, Red-Yellow Podzolic, and Latosolic Brown Podzolic soils), Ground-Water Laterite, Latosolic Rendzina, and Alluvial soils. Potentially the most productive of the soil groups are Reddish-Brown, Red and Earthy Red Latosols, some Alluvial soils and Reddish Prairie soils under irrigation. Soil groups of low potential productivity are the podzolic soils and Ground-Water Laterites.

Phosphorus is generally low in Latosols and most of them are strong phosphorus fixers. Generally, the values for total phosphorus are comparable to those for Red-Yellow Podzolic soils in the United States, but lower than those for the Gray-Brown Podzolic soils. Values for available phosphorus are very low according to the methods that were used. Until standards are developed in the Belgian Congo through field trials it would not be safe to use them as a basis for predicting fertilizer need. It must also be appreciated that all the total and available plant nutrients are low in Latosols.

Writing on the soils of the *Union of South Africa*, Van Garderen (1952) notes that the residual soils in the higher rainfall regions and the aeolian soils bordering on the Kalahari Desert are notoriously deficient in available phosphorus. This is reflected in the low phosphorus content of natural pastures and in the necessity for supplementing stock feeds with phosphates. The dearth of phosphorus is such that by Government regulation "no person shall use bonemeal or any bone product . . . for any purpose other than the feeding of livestock . . . "

As further noted by Van Garderen, with ever increasing demands for food, there have also been associated increased demands for fertilizer, predominately phosphorus. Consumption of superphosphate (16 to 20 per cent P_2O_5) increased from some 270,000 tons in 1939 to more than 455,000 tons in 1950. Approximately one-half of this is used for the production of corn, 25 per cent for wheat, and 25 per cent for other crops.

Fertilizer studies are conducted at most of the agricultural research stations throughout the country. The following are some of the more salient features of the results obtained (Van Garderen, 1952).

In growing corn under dry-land farming, the greatest relative increases in the yield of grain are generally associated with the lowest

rates of application. An annual application of 105 kg. superphosphate per hectare to corn grown each year on the same land (monoculture) increased the average yield of grain during a 20-year period from 1.7 to 2.0 tons per hectare.

Experimental evidence on the phosphorus requirements of wheat and other winter cereals is rather limited, except for the winter rainfall area of the Cape Province, where the annual application of 210 kg. superphosphate per hectare is generally advocated. Nitrogen, in conjunction with phosphorus, shows a more positive beneficial effect on wheat than it does on corn, particularly on old lands and sandy soils poorly supplied with humus.

A limited amount of alfalfa is raised under dry-land conditions. It is generally grown under irrigation. Alfalfa does not respond to phosphorus on the fertile Alluvial soils of Karoo and of the Orange River, which areas produce more than 50 per cent of the Union's total crop.

On the aeolian soils of the Vaal-Hartz and other irrigation areas, however, ample applications of soluble phosphate have been proved to be absolutely essential. Annual applications of approximately 530 kg. superphosphate per hectare are necessary to produce the optimum of 15.8 tons of alfalfa per hectare.

Potatoes and pastures respond well to applications of superphosphate under certain conditions and in association with nitrogen fertilizers.

All experimental evidence confirms the necessity of applying adequate amounts of phosphorus fertilizer for the production of more food in the Union of South Africa.

On the basis of such facts as can be obtained with no official estimates available, it is reasonable to suppose that Africa could use in the order of three to five times the present consumption of phosphorus, or 500,000 to 800,000 metric tons of P_2O_5 by the end of this decade.

c. Latin America. A striking characteristic of the agriculture of Latin America is the relatively small area of land in cultivated crops. The estimated total land area is 2058 million hectares (Food and Agriculture Organization of the United Nations, 1951a). Of this not more than 5 per cent is in cropland and only 3.1 per cent is cultivated annually. Most of the land is still covered with forests and woodlands with a higher percentage of waste land.

On the average there is 1.0 hectare under cultivation per head of farm population and only 0.63 hectare per head of total population. This is in comparison with an average of 0.52 hectare for the world total population.

To give some idea of the fertilizer needs, the crops grown in this

area are shown in Table VI for the years 1938–1939 and 1949–1950, and estimates are given for 1952–1953.

TABLE VI

AREAS OF 22 PRINCIPAL CROPS HARVESTED IN LATIN AMERICA[a]

Crop years	*Cereals*[b]	*Roots and tubers*[c]	*Sugar*	*Beans*	*Bananas*	*Oil seeds*[d]	*Coffee and cacao*	*Cotton and cotton seed*	*Tobacco*	*Total*	*Harvest per person*
					(million hectares)						
1938–1939	27.1	1.4	2.1	2.0	0.57	3.3	5.3	3.0	0.25	45.0	0.36
1949–1950	26.8	2.5	3.0	3.2	0.63	3.8	4.7	3.8	0.35	48.8	0.30
1952–1953	31.9	2.6	3.4	3.6	0.70	4.3	5.0	4.2	0.36	55.9	0.33

[a] Food and Agriculture Organization of the United Nations (1951a).
[b] Includes wheat, rye, maize, oats, barley, and rice.
[c] Includes potatoes, yucca, and sweet potatoes.
[d] Includes linseed, sunflower seed, peanuts, sesame, and castor beans.

It would be wrong to assume that the soil resources of Latin America are virtually unlimited. Much of the soil capable of easy cultivation has already been put to productive use. Much of the uncultivated land cannot readily be put under cultivation by private initiative alone because of the large capital investment required. Consequently governmental action is becoming increasingly important in the extension of the cultivated areas.

Besides increasing the arable area, the plans of many countries are to increase the crop yields per unit of land. Thus the efficient use of commercial fertilizers has a vitally important place in all such programs.

Next to nitrogen, which is needed particularly in the tropical regions, the most universal need over practically the whole of Latin America is for a more nearly adequate supply of phosphorus. From the vast majority of the experimental trials carried out to date in Latin America, it is obvious that phosphorus deficiency is a serious limiting factor in crop production, and that large quantities of this plant nutrient element will have to be used in every country to increase yields significantly on most soil types. Some alluvial and volcanic soils may be exceptions.

The consumption of commercial fertilizers in Latin America in 1950–1951 was 111,000 tons nitrogen (N); 110,600 tons P_2O_5; and 45,500 tons K_2O. This is approximately 1.8 kg. P_2O_5 per hectare of cultivated land. The consumption varies considerably, however, in different countries. Because of more nearly ample local supplies, con-

sumption per hectare is highest in Chile, followed by Peru and Cuba. All other Latin American countries use less than one kilogram per hectare. Fertilizers are used largely on high-value crops per hectare such as sugar cane, bananas, coffee, cotton, and potatoes. Much more phosphorus is needed in the production of pulses and cereals, which include wheat, corn, oats, barley, and rice (Food and Agriculture Organization of the United Nations, 1951a).

Three major kinds of evidence attest to the need for larger amounts of phosphorus in Latin American agriculture: (a) the soil groups; (b) the results of field experiments; and (c) the results of chemical tests on soils.

(a) The greater proportion of the soils of Latin America (Hardy, 1942, 1943) have undergone to a varying degree the process of laterization, and thus one finds soils which are generally very deficient in phosphorus. These soils cover most of Central America, most of Brazil, the Guianas, Venezuela, the eastern and very western parts of Colombia and Ecuador, Peru, Northern Bolivia, and Southeast Paraguay. They include such major soil groups as Latosols, Ground-Water Laterites, Red-Yellow Podzolic soils, etc. Other soils occur mixed with them, including highly productive young soils from recent volcanic deposits.

The degree of decomposition and eluviation of the wide range of rocks represented in Latin America varies greatly, depending on climate and length of time of exposure. In humid, tropical regions, for example in British Guiana, igneous and metamorphic rocks have given rise to residual soils the mineralogical composition of which differs greatly according to the nature of the original crystalline rocks. Thus, basic rocks (hornblende schists, diorite, dolorite, etc.) have given rise to fairly fertile red earths (Latosols) which are neutral to slightly acid, whereas acid rocks (granitic gniesses, granite, etc.) have weathered to thick masses of quartz-sand and kaolinitic clay which have developed into bleached, highly acid, infertile, silty, and sandy soils. These bleached soils occur in the Guianas and Brazilian highlands, in Venezuela and Bolivia. Large expanses of the red earths (Latosols) are found in Southwest Brazil.

In Uruguay, Paraguay, Southern Bolivia, and Northern Argentina are found the soil groups which develop under drier climatic conditions, such as Chernozems or black earths, and Reddish-Chestnut, Chestnut, and Brown soils.

Chestnut soils occur in the central part of Chile and southern part of Argentina (Western Patagonia). Soils of the Mountains and Mountain Valleys are distributed in Mexico, Guatemala, El Salvador, and the Andes, which run from north to south of the South American con-

tinent near the western coast. Desert soils are found in Mexico, Peru, Chile, and Argentina (Patagonian Plateau), and Gray-Brown Podzolic soils in Chile and Argentina.

Alluvial soils occupy large areas of riverain and coastal country, but their widest distribution occurs in the Amazon Basin and Parana Valley.

(b) Field experimental work has been conducted in various parts of Latin America. It is fully recognized, however, that in relation to the large areas involved, much more needs to be done. It is significant that even the more productive soils, such as the black earths found in Uruguay, give responses to phosphorus. Alfalfa (International Bank for Reconstruction and Development and the Food and Agriculture Organization of the United Nations, 1951, pp. 6, 41, 42) has shown marked responses to phosphorus in a number of field experiments on soils in Canelones and Colonia conducted by the Agricultural Experiment Station at Estanzuela and by the Institute of Industrial Chemistry. Recently at Estanzuela superphosphate increased the yield of alfalfa-rye grass mixture over three and one-half times. Present evidence, based on field and laboratory tests, indicates that at least one-half and possibly three-fourths of the soils of Uruguay should receive phosphorus fertilizer for the successful growth of alfalfa.

In Chile, for instance (Ignatieff *et al.*, 1949, p. 75), experiments have been conducted with wheat on different soil types at thirteen experiment stations. At five of these stations increases in yields were secured with phosphorus; at another four nitrogen was the most important plant nutrient; and at two other stations both nitrogen and phosphorus were needed. At two stations no significant increases were obtained with nitrogen, phosphorus, and potassium applied singly or in combination.

In Brazil, experiments conducted with wheat have also shown the need for phosphorus. In Guatemala potatoes are grown in some of the high mountain valleys. In rotation with potatoes, legumes necessary to maintain soil fertility are planted. For legumes, superphosphate is essential; without it, growth is very poor.

(c) Laboratory methods of testing soils are also in use in many Latin American countries. Chemical tests of soils in Latin America confirm the results of field experiments, *viz.*, that many soils need additional phosphorus to maintain crop and food production at adequate levels.

In Latin America there are approximately 32 million hectares of cereals (wheat, rye, corn, oats, barley, and rice) besides some millions of hectares of roots, tubers, beans, and other crops. The present average

rate of application is approximately only 1.8 kg. P_2O_5 per hectare of cropped land. It is therefore suggested that a reasonable appraisal of need by 1960 for Latin America would be about 600,000 tons P_2O_5 from commercial sources, which would provide for an average rate of application of approximately 10 kg. P_2O_5 per hectare.

d. Oceania. Australia is a very old land in the geologic sense and many of the soils are exceedingly leached, some under more tropical conditions than now exist. With a few exceptions the soils of Australia (Bulcock, 1952; and Stephens, 1952) are notoriously deficient in phosphorus. Many soil types in South Australia and in parts of western Australia also require the application of copper, molybdenum, and zinc for the good growth of legumes. "Nitrogen may also be limiting, but except for the use of nitrogen fertilizer on stubble-sown oats and barley, it has been found more economical to use peas and legumes to replenish the soil nitrogen than to apply nitrogen fertilizers."

Before phosphorus came into common usage, Australia imported hard wheats. Now this country is one of the major wheat exporters, as a result of phosphate fertilization, although production has fallen off recently for economic reasons.

The poor native grasses of coastal Australia carry about one ewe per hectare. The introduction of legumes and good-quality grasses, which has been made possible by the use of phosphorus, has increased the carrying capacity of sown pastures up to seven or eight ewes per hectare.

In Australia, phosphorus applications are required by nearly all crops, including fruits, vegetables, cereals, linseed, intensive pastures, and sugar cane. The usual application of superphosphate is approximately 100 kg. per hectare (22 kg. P_2O_5). Applications tend to fall below this value for wheat, especially in the areas of lowest rainfall, and to rise above it, to maximum dressings of approximately 250 kg. per hectare, in the case of sown pasture where water is reasonably abundant. Vegetables and potatoes receive larger applications.

Approximately 90 per cent of the fertilizer used in Australia is superphosphate. A great proportion of it is used on seeded pastures of subterranean clover with various grasses on podzolic and lateritic podzolic soils in southern, eastern, and southwestern Australia, and on the red loams (Latosols) of northeastern Australia. However, the superphosphate used on the podzolic soils is predominantly applied to pastures and sown crops in Tasmania, Victoria, and New South Wales rather than to sugar cane and other crops as on the soils in Queensland. Superphosphate is also used in considerable amounts on the wheat crop on soils which are termed red-brown earth and mallee (the equivalent of Reddish-Chestnut and slightly saline Reddish-Brown soils).

Phosphorus is not used to any extent on the heavy-textured black earths of eastern Australia that contain up to 0.4 per cent phosphorus. These soils are used to a fairly large extent for pasture and wheat production. There is a limited use of superphosphate on alfalfa when irrigated and on some of the other great soil groups which are used to a limited extent for crop production.

In *New Zealand*, though mature soils do occur (Wild, 1945, p. 58), the greater proportion of the soils are still young, and characteristics of the parent material have a pronounced influence on the properties of the soils. On the basis of the parent material, the New Zealand soils can be classified as alluvial soils, volcanic ash soils, limestone soils, papua soils (blue calcareous soils), greywacke soils, and swamp soils. The limestone and the papua soils have the highest natural fertility. Many of the soils from volcanic ash are deficient in plant nutrients, particularly phosphorus, and some of these soil types are too low in cobalt. Many of the soils from mudstones are notoriously low in phosphorus.

The outstanding feature of New Zealand soils is their need of phosphorus fertilizers. Increased yields from phosphorus are obtained with almost all crops on almost all soil types. In fact, some of the greatest responses to phosphorus on ranges in the world are reported from New Zealand. Hill pastures are now quite commonly treated with phosphorus fertilizers by aircraft. Some of the soils, particularly in North Auckland, are high phosphorus "fixers." In the case of swedes and turnips (Wild, 1945, p. 54), as little as 100 kg. of superphosphate per hectare makes all the difference between no crop at all and a good crop. On pastures, especially in the moister parts of the North Island, the effect of a dressing of basic slag, superphosphate, or superphosphate and lime is phenomenal. For potatoes, mangolds, and generally for all root and fodder crops, phosphorus is essential, and there is no doubt of the good results obtained with this plant nutrient element even on cereals such as wheat and oats. Superphosphate accounts for 90 per cent of the total fertilizers normally used in New Zealand. In bringing new pumice (volcanic ash) country under cultivation (Wild, 1945, p. 37; Saxby, 1948, p. 125; Ignatieff, 1949, p. 18) as much as 1150 kg. per hectare of superphosphate is used, if available, at time of sowing the pastures. Usually 375 kg. per hectare are applied at seeding in the fall, 375 kg. as top-dressing the following spring, and 375 kg. the following autumn. Thereafter, annual dressings of 375 kg. per hectare are sufficient to maintain a good production level. Italian rye grass and white clover make the best sown pastures. On soil types not markedly deficient in phosphorus (Wild, 1945, p. 171), yearly applications of 125 to 250 kg. of superphosphate per hectare are deemed to be sufficient; for turnips

and swedes, 200 to 300 kg.; for cereals, 125 to 250 kg.; for potatoes, 375 to 525 kg.; and for peas, beans, and vetch, 125 to 375 kg. of superphosphate per hectare.

New Zealand (New Zealand Government, 1952) is the largest exporter of dairy products, the second largest exporter of wool, and one of the largest exporters of meat. This country has great potentialities for expanding food production and is making extensive efforts to develop these resources. A recent careful survey of the food-producing potential of New Zealand indicates that, provided the necessary fertilizers are available, it will be possible to increase farm livestock numbers by 30 per cent during the next two decades. A large expanse of some 9 million hectares of occupied but unimproved hill country is capable of being improved, and this is systematically being surveyed and developed. The scope for developing hilly country has been increased considerably by aerial top-dressing methods which now account for the spreading of 7 to 10 per cent of all fertilizer used in New Zealand. If fertilizers were more freely available, an expanded program of top-dressing hilly soils with phosphorus fertilizer would be undertaken. In pasture improvement, the less rolling (but unplowable) hills are cleared and oversown with improved strains of grasses and clover and the land top-dressed with phosphorus. This treatment will increase the carrying capacity by 200 to 300 per cent. Where the land is too steep for surface cultivation, the pastures are oversown with clovers and top-dressed with phosphorus fertilizer. Such a treatment increases the carrying capacity by 100 to 150 per cent. Virgin land that could be plowed principally for dairy farming could be expanded to 40,000 or 60,000 hectares annually if phosphorus fertilizers were more freely available.

In considering the agronomic phosphorus needs of Oceania as a whole, it is probably reasonable to suggest that by 1960 this region could use 900 thousand tons P_2O_5 if this quantity of phosphate fertilizer were available.

e. Europe. The agricultural area of Europe (exclusive of the U.S.S.R.) is 248,000,000 hectares. Of this total (Food and Agriculture Organization of the United Nations, 1951b) 148,000,000 are arable, including orchards and fallow, and 100,000,000 hectares are in permanent pasture. The chief crops grown are 75.2 million hectares of cereals—wheat, rye, oats, barely, corn, and mixed grains in the order noted; 9.5 million hectares of potatoes; 6.3 million hectares of grapes; 3.1 million hectares of dry beans; and 2.3 million hectares of sugar beets. Smaller acreages of other crops, including peas, broad beans, oil seeds, cotton, chick peas, lentils, grapes, millet, and sorghum, orchard crops, rice, citrus fruit, etc., are also grown.

In the year ending June 30, 1951, 2,534,881 tons of P_2O_5 were used. The general pattern of consumption is that the largest amounts of phosphorus fertilizer are used on cereals, especially wheat, and smaller amounts are used on potatoes, sugar beets, vegetables, other tilled crops, and horticultural crops. A relatively smaller amount of the total consumption is used on grassland. This pattern of consumption varies considerably from one country or region to another. More detailed usage in two typical countries is given later on in this section.

The place of commercial fertilizers in the agriculture of Europe, with particular emphasis upon the factors affecting consumption, is being intensively studied by several European countries as members of international organizations. The need for a larger and more efficient use of commercial fertilizers as one means of increasing crop and food production is being strongly recommended. As investigations on the status of consumption are already under way and as participating countries have approved current reports, a brief reference to such work will clarify the position of commercial fertilizers in European agriculture. It should be noted that in Europe about half of the plant nutrients used in crop production are supplied from organic sources such as farm manures. The study of chemical fertilizers alone does not, therefore, present a balanced picture, although it is a vital and increasingly important part of all crop production programs.

A report by the Organization for European Economic Cooperation (1950) on the use of fertilizers emphasizes that, with a limited agricultural area, an increase in agricultural production must of necessity, in the first place, come from intensifying production in the existing areas. Together with good farm practices, high productivity can be achieved by an increased and more efficient use of commercial fertilizers. The report further notes that the use of such fertilizers will also help in the greater production of animal manures. It says:

"In the cycle of fertility, the use of commercial fertilizers plays a most important part, resulting not only in a higher production of market crops but also of fodder, providing for a greater number of livestock or improved feeding of existing stock, on which follows an increased availability of plant nutrients in a particularly suitable form for both soils and plants."

In a continent where fertilizers have been used for such a long period, it is inevitable that consumption patterns vary considerably from one country to another. In appraising the present and potential need for chemical phosphoric acid, the position will be more clearly understood if the two chief patterns are briefly described.

One characteristic of the use of phosphorus in Europe as a whole is that in many countries, in comparison with the use of nitrogen and

potassium, the use of phosphorus is relatively low in contrast to its use in North America. For instance, in 1950–1951 Germany used 361,600 tons of nitrogen, 411,400 tons of P_2O_5, and 659,000 tons of K_2O. This is characteristic of several countries.

The relatively low consumption of phosphorus, especially in relation to potassium, in some countries is due to the fact that Europe produces nitrogen and potassium fertilizers largely from indigenous materials and in excess of her needs, whereas phosphorus fertilizers are manufactured from imported rock. The cost per unit of chemical phosphoric acid is often higher than the cost of a unit of potash.

Despite these economic factors, however, there are sound agronomic reasons for using potassium in larger amounts in some areas. To the south of the Baltic, lying east and west, are large and important areas of organic soils. Potatoes and sugarbeets are important crops. Both the kinds of the soil and the crop demand large tonnages of potassium for maximum production. South of the organic soils are the soils of the temperate grasslands and forest lands in Central and Southern Europe, which require essentially phosphorus, especially when planted to cereal crops. In northern Europe are the soils of the temperate forests requiring phosphorus, possibly more than any other element, especially if nitrogen is provided from legumes and manures. In southeastern Europe are found the soils of the temperate grasslands, which also require phosphorus.

These basic variations in soils and crops are roughly related to the pattern of fertilizer consumption in different countries. For example, Belgium, Denmark, the Netherlands, and Germany, all with large and important areas of organic soils, use much more potassium than phosphorus. Total consumption in 1950–1951 was 700,100 tons of P_2O_5 and 1,019,000 tons of K_2O. In contrast, the United Kingdom, Sweden, and Finland used 546,200 tons of P_2O_5 and 215,600 tons of K_2O in the same year. Switzerland and Italy together consumed 330,000 tons of P_2O_5 and only 32,000 tons of K_2O in 1950–1951. The consumption in the Netherlands and Italy is noted as typical of the use of phosphorus in different areas. In the Netherlands, consumption is estimated to be approximately 120,000 tons of P_2O_5, which is used as follows: cereals, 21 per cent; potatoes, 14 per cent; sugarbeets, 3 per cent; tubers, 3 per cent; various others, 24 per cent; and grassland, 35 per cent. For tillage crops, 60 kg. P_2O_5 is applied per hectare; for horticultural crops, 90 kg.; and for grassland, 40 kg.

In Italy approximately 7 million hectares of cereals are the mainstay of the food supply. Wheat occupies 4.7 million hectares and maize 1.2 million hectares. Half the phosphorus supply of 240,000 tons of

P_2O_5 is used on wheat. An estimated 18 per cent is used on grassland and the remainder on other crops.

An area of low use of phosphorus from commercial fertilizers is that in Eastern Europe. In Eastern Germany the available supply of phosphorus from indigenous sources and imports is estimated at 66,000 tons P_2O_5 in 1950–1951. This tonnage provided approximately 10 kg. per hectare of agricultural land in Eastern Germany, whereas the real need is much higher, possibly three times as much. If the same rate of consumption holds true for the countries of Eastern Europe, the consumption of phosphorus is low and the potential need is relatively high. Consumption targets for all fertilizers have been set up for countries of the Organization for European Economic Cooperation (1950) as part of the present program of increasing agricultural production. These countries are: Austria, Belgium, Denmark, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, The Netherlands, Norway, Portugal, Sweden, Switzerland, Trieste, Turkey, and the United Kingdom. These targets project an overall increase in consumption for all fertilizers of about 86 per cent higher than prewar use, to be attained by 1952–1953. Within this overall total a consumption of 2,928,000 tons of P_2O_5 is set up for the Organization for European Economic Cooperation countries. All countries in Europe (excluding the U.S.S.R.) in 1950–1951 consumed about 2,534,800 tons P_2O_5. In some countries consumption is relatively low. Seventy-five million acres of cereals are vital to the food production of Europe. Much of this acreage requires more phosphorus, as do 100,000,000 acres of grassland.

In the light of the preceding discussion, an increase in Europe of 50 per cent in present consumption of 2,487,000 tons by 1960 or a total consumption by that year of some 3,700,000 tons of P_2O_5 is not considered unreasonable.

f. Northern America (Canada and the United States). The crop area of Canada and the United States is 517,912,000 hectares, of which 220,488,000 hectares are arable land, including fallow and orchards, and 297,424,000 hectares are permanent meadows and pastures. The climatic range is from arctic to subtropical.

With other necessary fertilizers, the following tonnages of phosphorus fertilizers were used on the crops noted in 1950–1951. In the United States, 2,044,924 tons P_2O_5 were used on twenty-one crops (Fertilizer Work Group, 1951). In thousands of tons the chief fertilized crops were: corn, 442; pastures, 360; hay, 229; wheat, 220; oats, 162; vegetables, 163; cotton, 138; and 331 on fourteen other crops.

The potential phosphorus fertilizer need of the United States is presented by Parker in Chapter XIII; therefore, only a few general

statements in regard to this country need be made. The United States can be conveniently subdivided into five soil regions. The soils of the North and Temperate Forest Region, the Podzols and podzolic soils, and those of the Warm-Temperate Forest Region, the Red-Yellow Podzolic, and associated soils are naturally deficient in phosphorus. There are, however, notable exceptions, as for instance the bluegrass region of Kentucky, the Central Basin of Tennessee, and the Alluvial and loessial soils of East Tennessee and Mississippi, which are relatively high in available phosphorus. In the third soil region, that of the Temperate to Warm-Temperate Grassland, the Prairie soils, although naturally fertile for sustained cropping, need phosphorus, as do some of the soil types in the Chernozem belt, and especially so when irrigated. This also applies to the Brown, Chestnut, and Reddish-Chestnut soils.

The soils of the desert region, when irrigated, as a general rule give good responses to phosphorus but the more soluble forms of phosphorus fertilizers have to be used. The soils of the mountains and mountain valleys comprise a great variety of soils with greatly varying phosphorus content and crop responses (Kellogg, 1941).

Parker in Chapter XIII states that the 1955 goal of 3,429,000 metric tons P_2O_5 for phosphorus fertilizer consumption seems adequate for the United States crop production goals and for substantial improvement in the phosphorus fertility of the soils.

The Canadian agricultural soils vary considerably in their morphological and chemical characteristics (Stobbe, 1952). In Eastern Canada and British Columbia acid Podzol and Brown Podzolic soils and associated poorly drained and Alluvial soils are used extensively for crop production, whereas in southern Ontario Gray-Brown Podzolic soils form the dominant agricultural land. In the Grassland region of the three Prairie Provinces, Brown, Dark Brown, and Black soils form definite belts as one proceeds from the dry to the more moist climatic zones. In the northern forested region of these three provinces Gray-Wooded soils are increasingly utilized for agricultural production.

Phosphorus is limiting for maximum production on most of these soils. On the Podzol, Brown Podzolic, and Gray-Wooded soils phosphorus fertilizers almost consistently give yield responses. In addition, most Gray-Brown Podzolic soils, unless heavily manured, respond to phosphorus applications. The response to applied phosphorus on the Black, Dark Brown, and Brown soils of the Grassland region depends on the moisture supply. Crop increases from phosphorus are generally obtained on summer-fallowed land in the case of the less arid soils, but in the Brown soil region increases are obtained only under favorable con-

ditions, using summer-fallow on heavy soils, or under irrigation. There is a considerable variation in the response to phosphorus among the different soils belonging to the same general group.

In the last ten-year period the tonnage of phosphorus utilized for fertilizer purposes in Canada was more than trebled. The following amounts of P_2O_5 in thousands of tons were used in 1950–1951: in the eastern zone, 78 for potatoes, tobacco, vegetables, fruits, etc.; in the prairies, 40, almost entirely on cereals; and on the Pacific Coast, 5, for general crops. No estimation of the possible phosphorus fertilizer need in Canada by the end of this decade has been observed in reports or literature, but on the basis of agronomic needs it might be suggested that the consumption could be in the order of 165,000 metric tons of P_2O_5 per annum.

From all the foregoing it is estimated that by 1960 about 3,600,000 metric tons of P_2O_5 for Northern America is not an unreasonable appraisal of the need for phosphorus.

4. Conclusions

A larger crop and food production, especially in the industrially under-developed regions, requires the use of much more phosphorus than the 5.7 million tons P_2O_5 used in 1950–1951. That this supply is of growing importance in the world's agriculture is attested by the fact that the world consumption of phosphorus fertilizer has increased approximately 1.8 million tons P_2O_5 from 1946–1947 to 1950–1951. Every continent has contributed its share to this increase.

In fact so rapid has been this increase in consumption that the supply of high-grade raw materials, particularly of native or elemental sulfur, has not kept pace with world demand. As a result, during the last two years, the use of phosphorus has been limited to some extent by the available supply.

Despite these difficulties, which will eventually be overcome, there is no doubt that the world need for phosphorus is much higher than the consumption of 5.7 million tons of P_2O_5 in fertilizer year 1950–1951. Based on considerations of the soils on which the major crops are grown, crop responses to phosphorus, the current rate of world increase in consumption, increases in food needs for growing populations, the maintenance of higher levels of human nutrition and other factors, it is estimated that in the order of 11 million tons P_2O_5 could be usefully used by 1960, were that tonnage available and this rate of consumption possible.

The efficient use of fertilizers depends upon efficient soil management. But the possibilities for better husbandry in any country are

TABLE VII

PRESENT PHOSPHORUS FERTILIZER CONSUMPTION AND POTENTIAL NEEDS BY 1960

Continent	*1950–1951*	*1959–1960*
	(Thousand metric tons)	
Asia	295	1,400
Africa	144	800
Latin America	111	600
Oceania	490	900
Europe	2,535	3,700
North America	2,133	3,600
World Total	5,708	11,000

ultimately associated with the development of the economy as a whole. Thus we must expect the actual use of fertilizer to depend not only on the needs of the soils and crops but also on the general level of economic activity. Even where phosphorus fertilizer needs are demonstratively great, large increases in use will only come along with the general economic and social development. These two factors are outside the scope of this paper. Nevertheless, as a measure of the total amount of phosphorus fertilizer that could be gainfully used, if world conditions permitted its use, 11 million tons P_2O_5 is suggested as a reasonable future world target.

IV. ACKNOWLEDGMENTS

The authors wish to thank all those who have given valuable services and advice and assistance, and particularly Frank W. Bulcock, Australia House, London; M. S. du Toit, Director of Technical Services in the Union of South Africa; Herbert Greene, Rothamsted Experiment Station, Harpenden, England; Charles E. Kellogg, United States Department of Agriculture; F. W. Parker, United States Department of Agriculture; W. H. Pierre, Iowa State College, Ames, Iowa; Guy D. Smith, United States Department of Agriculture; C. G. Stephens, Council of Scientific and Industrial Research, Melbourne, Australia; P. C. Stobbe, Department of Agriculture, Ottawa, Canada; J. van Garderen and the Division of Chemical Services, Pretoria, Union of South Africa; and D. W. Woodward, New Zealand Embassy, Washington, D. C.

REFERENCES

BIRCH, H. F. 1951. Phosphate Investigations. Annual Report, pp. 62–64. East African Agriculture and Forestry Research Organization. East Africa High Commission. Nairobi.

BULCOCK, F. W. 1952. Phosphorus Fertilizer in Australia. Manuscript. Australia House, London.

FERTILIZER WORK GROUP, NATIONAL SOIL and FERTILIZER RESEARCH COMMITTEE. 1951. Fertilizer Use and Crop Yields in the United States. Bept. No. 5, Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1946. World Fertilizer Production and Consumption and Targets for the Future. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1947. Fertilizer Review. Third Session. FAO Conference, Geneva.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1949. Fertilizers. Commodity Series, Bull. No. 17. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1950a. Fertilizers. Commodity Report. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1950b. Yearbook of Food and Agricultural Statistics. 1949. 1. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1951a. The Latin American Fertilizer Supply and Resources for Improving the Supply. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1951b. Yearbook of Food and Agricultural Statistics. 1950. Washington, D. C.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1951c. Fertilizers: a World Report on Production and Consumption. Rome, Italy.

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1952. Fertilizers—A World Report on Production and Consumption. Rome, Italy.

GRACIE, D. S., and KHALIL, F. 1948. The Total and Available Phosphoric Acid in Egyptian Soils and the Effect of Superphosphate on the Main Agricultural Crops. Ministry of Agriculture, Egypt. Technical and Scientific Service, Chemical Section, Bulletin No. 251, pp. 1–72. Government Press, Cairo, Egypt.

GREENWOOD, M. 1951. Fertilizer Trials with Groundnuts in Northern Nigeria. *Empire J. Exptl. Agr.* **19**: 225–241.

HARDY, F. 1942–1943. The Soils of South America. *Chronica Botan.* **7**: 211–217.

HOYLE, S. T., JACKSON, R. A., and DISNEY, F. J. 1951. Agricultural Research Station, Nyasaland Protectorate. Report of the Department of Agriculture for the Year 1949. Part II, pp. 13–14. Government Printer, Zamba.

HOYLE, S. T., JACKSON, R. A., and DISNEY, F. J. 1952. Agricultural Research Station, Nyasaland Protectorate. Report of the Department of Agriculture for the Year 1950. Part II, pp. 19–22. Government Printer, Zamba.

IGNATIEFF, V., Editor. 1949. Efficient Use of Fertilizers. Food and Agriculture Organization of the United Nations, Washington, D. C.

IGNATIEFF, V. 1951. Results of Experiments and Practical Experience in the Use of Fertilizers, Manures and Soil Amendments with Rice. Food and Agriculture Organization of the United Nations, Washington, D. C.

INTERNATIONAL BANK FOR RECONSTRUCTION AND DEVELOPMENT AND FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS. 1951. The Agricultural Development of Uruguay. Report of a Mission sponsored by the International Bank for Reconstruction and Development (Washington, D. C.) and the Food and Agriculture Organization of the United Nations (Rome, Italy) at the request of the Government of Uruguay.

KELLOGG, C. E. 1941. The Soils That Support Us. The Macmillan Company, New York.

KELLOGG, C. E., and DAVOL, F. D. 1949. An exploratory study of soil groups in the

Belgian Congo. *Publication de l'Institut National pour l'Etude Agronomique du Congo Belge (I. N. E. A. C.) Serie Scientifique* 46.

KELLOGG, C. E. and ORVEDAL, A. C. 1950. World Food Possibilities and Fertility Status of our Soils. Chapter 1, Mineral Nutrition of Plants. The University of Wisconsin Press, Madison, Wisconsin.

MCEWEN, T. 1932. Notes on Fertilizer Trials, 1928–1932. Second Annual Bulletin of the Department of Agriculture, pp. 16–20. Government Printer, Livingstone, Northern Rhodesia.

NEW ZEALAND GOVERNMENT. 1952. New Zealand's Sulphur Requirements. Statement.

NYE, P. H. 1952. A Survey of the Value of Fertilizers to the Food Farming Areas of the Gold Coast. 1950. University College, Ibadan, Nigeria.

ORGANIZATION FOR EUROPEAN ECONOMIC COOPERATION (SUB-COMMITTEE ON FERTILIZERS, FUNGICIDES, AND INSECTICIDES). 1950. Report, Fertilizers in Agricultural Recovery Programmes.

RATTRAY, A. G. H. 1951. Maize, hints for the new farmer. *Rhodesia Agr. J.* 48: 123–134.

SAXBY, S. H. 1948. Pasture Production in New Zealand, p. 125. The Department of Agriculture, Wellington, New Zealand.

STEPHENS, C. G. 1952. The Use of Phosphorus Fertilizers in Australia. Manuscript. Council of Scientific and Industrial Research, Melbourne, Australia.

STEWART, A. B. 1947. Report on Soil Fertility Investigations in India with Special Reference to Manuring. Printed in the Army Press, Delhi.

STOBBE, P. C. 1952. The Use of Phosphorus Fertilizers in Canada. Manuscript. Department of Agriculture, Ottawa, Canada.

SUPREME COMMAND FOR ALLIED POWERS, JAPAN. 1947a. Field Experiments with Fertilizers in Japan. General Headquarters, Supreme Commander for Allied Powers, Natural Resources Section, Rept. No. 86, Tokyo.

SUPREME COMMAND FOR ALLIED POWERS, JAPAN. 1947b. Fertilizer Practices in Japan, General Headquarters, Supreme Commander for Allied Powers, Natural Resources Section, Rept. No. 93, Tokyo.

SWANSON, C. L. W. 1946. Reconnaissance soil survey of Japan. *Soil Sci. Soc. Amer. Proc.* 2: 493–507.

VAN GARDEREN, J. 1952. Extracted from a report of the Division of Chemical Services of the Union of South Africa by courtesy of M. S. du Toit, Director of Technical Services in the Union of South Africa.

WILD, L. J. 1945. Soils and Manures of New Zealand. 4th ed. Whitcombe and Tombs, Ltd., Christchurch, New Zealand.

WORKING PARTY ON FERTILIZERS OF THE INTERNATIONAL RICE COMMISSION. 1951. Report of the First Meeting of the Working Party on Fertilizers. FAO Development Paper No. 11. Agriculture. Food and Agriculture Organization of the United Nations, Rome, Italy.

YAO, K. K. 1948. Fertilizers in China. Food and Agriculture Organization of the United Nations, Washington, D. C.

INDEX

A

A value (Fried & Dean), 50–52, 111, 112, 113, 165, 174, 402
Acid soils, effects of lime on crop yields, 283–286
Adenylic acid, 18–19
Ammonia, distribution in fertilizer manufacture, 390
  treatment of superphosphate, 390–391
Ammoniated superphosphates, 230–231, 236, 324, 325–327, 331–333
Ammoniation of ordinary superphosphate, 228–229
  of concentrated superphosphate, 227–228
Ammonium phosphates, 224, 236, 301, 305, 381–382
Ammonium citrate method, 314–316, 317–322
Anion exchange in soils, 73–76
Apatite, 66–67, 154, 347, 350–352, 378, 397
Arsenate exchange, 73
Available phosphorus, critical level, 169
  as index of nutrient value, 330–337
  soil tests for, 153–183
Azotobacter method, for phosphate availability, 166, 328

B

b value (Mitscherlich), 48
Basic slag, 220, 303, 306, 382, 433, 434, 452–454
  phosphorus availability, 220, 221, 235
Bone meal, 221, 235

C

Calcined phosphates, 216–217, 235, 333
Calcium-magnesium-phosphate, 383
Calcium metaphosphate, 217, 235, 382–383
  crop responses, 217, 218, 219
Calcium metaphosphate glass, 301, 305, 308, 334–335
Calcium orthophosphates, 300, 302, 303
Calcium phosphates, 91–94, 95, 96, 99, 100
  basic, 310–312
Calcium sulfate, 398
Carbonate-apatite, 90, 94, 95
Carbon dioxide and availability of soil phosphorus, 248, 250
Cation exchange-anion exchange ratios, 171–172, 174
Citric acid method, 316, 317–322
Clay minerals, effects on phosphate retention, 73, 77
  reaction with phosphates, 105–106
Concentrated superphosphate, 191, 201, 212, 216, 226, 234
Contact exchange, 55
Crop growth, correlation with soil tests, 166–172, 178
  relation to phosphorus level, 166–169, 170, 172, 178, 183
Crop residues, phosphorus availability, 244–246
Crop utilization of phosphorus forms, 78–79
Crystallinity of phosphate fertilizer materials, 302, 305–306
Cunninghamella method, for phosphate availability, 166, 328, 329

D

Deep tillage, 268
Defluorinated rock phosphate, 214, 333, 334, *see also* Calcined phosphates, Fused tricalcium phosphate
Dicalcium phosphate, 212, 213, 235, 300, 302

E

Evaluation of phosphate fertilizers, alkaline ammonium citrate extraction, 316, 317–322
Azotobacter method, 328
biological methods, 328–330
citric acid extraction, 316–322
Cunninghamella method, 328, 329
extraction methods, 314–322
field experiments, 190–232, 431–435
history, 313–317
laboratory methods, 313–330
Neubauer method, 329, 330
neutral ammonium citrate extraction, 314–316, 317–322
tracer technique, 49–52, 232–233
water extraction, 314, 317–322
Evaluation of soil-testing methods, biological, 174–175
chemical extraction, 173–174
Extractable phosphate, 113–115

F

Farmyard manure, availability of phosphorus, 246–247, 431–432
reducing phosphorus fixation, 251
Feeding power of plants, 54–56, 196
Ferrophosphorus, 382, 399
Fertilizer phosphorus, absorption rate, 45–46
influence on growth and yield, 47–48, 232–233
influence on composition, 48–49
Fertilizers, band placement, 441, 442
caking of, 393–394
consumption in Great Britain, 429–431
drillability, 393–394
granulation, 394–395
particle size, 393
Filter cake, byproduct from sodium phosphate, 398
Fineness of phosphate fertilizer materials, 306–312, 334, 335
Fixation of applied phosphorus, 250–251, 255–258
Flavin nucleotides, 20–22
Fluorapatite, 194, 195, 300, 301, 352, 353, 378
Fluorine, byproduct from phosphate manufacture, 397
Forms of phosphorus in soils, biologically available, 153–154, 164–166
chemically soluble, 153–154, 161–164
Fused tricalcium phosphate, 305, 308, 333, 334, 382–383, *see also* Defluorinated rock phosphate
crop response, 214, 215, 235
fluorine content, 214
particle size, 214

G

Green manures, availability of phosphorus, 244–246
Growth curves, 47–48
Guano, 354–355

H

Humus extracts, solubility of soil phosphorus, 248
Hydrated sesquioxides, reactions with phosphate, 70, 75
Hydroxylapatite, 90, 91, 92, 93, 95, 116, 154, 195, 301, 378

L

Land utilization, in Great Britain, 427–429
Lecithin, 224
Liming, effects on phosphate availability, 281–296
effects on phosphorus in crops, 286–287
Liquid phosphoric acid, 223, 236

M

Marling, 282
Microbiological transformations of phosphorus, 244, 245
Monocalcium phosphate, 300
Movement of phosphorus in soil, 261

N

Neubauer method, for evaluating phosphate fertilizers, 329, 330
Nitric phosphates, analyses, 389
as phosphorus sources, 225, 227, 236
production processes, 387–390
relationship to fixed-nitrogen industry, 389, 391
Nitrogen fertilizers, effect on soil pH, 104
Normal superphosphate, 324, 325, *see also* Superphosphate
Nucleic acids, 133–135, 154, 223
Nucleoproteins, 16–18
Nutrient value of phosphate fertilizers, 330–337

O

Ordinary superphosphate, 378–381, *see* Superphosphate
Organic anions, effect on phosphorus uptake, 249
increasing phosphorus solubility, 249–250
Organic materials, phosphorus supplied by, 244–247
Organic phosphates, availability of, 223, 224
in soil, 90, 404–406

P

Phosphate, absorption by plants, 6–8
bond energy, 18, 24–26, 37–38
in cell sap, 1, 2
deposits, domestic, 347–371
Florida hard-rock field, 362–363
Florida land-pebble field, 357–362
Tennessee brown-rock field, 363–364
distribution in plants, 9–12
extractable, 113–115
fertilizers, *see* Phosphorus fertilizers
fertilizer materials, citric acid solubility, 318, 336
degree of crystallinity, 302, 305–306
fineness, 306–312, 334, 335
specific surface, 309–310
variability, 302–312
water-solubility, 300, 301, 306, 325–327
fixation, 67–72, 79–80, 435–438
in glycolysis, 28–31
ions, rate of reaction in soil, 76
minerals in soils, 68, 71
miscellaneous, availability to plants, 224, 236
reactions in soils, 67, 70, 71, 74, 76
rock,
definition, 377–378
production in U.S., 358
resources and reserves in U.S., 358, 364–368, 370–371
solubility, 301, 308, 335–337
world sources and production, 452, 454
see Rock phosphate
role, in carbohydrate breakdown, 28–32
in carbohydrate synthesis, 32–37
in photosynthesis, 33–37
solubility, effect of pH, 101–104
effect of Ca^{++} activity, 103–104
effect of $CaCO_3$, 104–105
tailing, disposal problems, 397–398
utilization, by crops, 78–79
water-soluble in soils, 1–6
Phosphatized rock, 354
Phospholipids, 12–13, 132–133
Phosphoric acid, dissociation constants, 94
production from phosphorus, 385–386
world production, 189
Phosphorites, marine, 352–353
residual, 353
Phosphorus, absorption by plants, 1–8
amount of, 43–44
influence of soil and fertilizer phosphorus, 45–46, 52–56
absorption processes, contact effects, contact, 54–55
description of system, 53
availability, development of soil tests for, 155–166
effects of soil management, 243–273
content of crops, 443
cycle, 291–294
deficiency symptoms, 12
electric furnace, 385
in energy transfers, 24–37

fertilizers, *see* Phosphorus fertilizers
fixation, 250–251, 255–258, 289–291
forms in plants, 293
organic, amounts in soils, 131–132
determination in soils, 123–131
differentiation from inorganic phosphorus in soils, 123–125
distribution in soil profiles, 131–132
forms in soils, 132–136
importance in plant nutrition, 141–144
inositol phosphates in soils, 135–136
mineralization in soils, 137–141
nucleic acids in soils, 133–134
phospholipids in soils, 132–133
stabilization in soils, 136–137
placement, *see* Placement of phosphorus
requirements of U. S. soils, 419–424
responses in field experiments, 431
in soils, *see* Soil phosphorus
subsoil, *see* Subsoil phosphorus
Phosphorus fertilizer, citric acid solubility, 318, 336, 434, 435
comparison of availability determinations, 232, 233
consumption in Europe, 480–481
effectiveness of different forms, 432–435
effects of liming, 443–445
efficient utilization, 446
evaluation, by biological methods, 328–330
by extraction methods, 314–322
by laboratory methods, 313–330
frequency of application, in rotations, 256–257
to pasture, 257
granular, 435
laboratory evaluation, 299–340
methods of application, 440–443
neutral citrate solubility, 301, 303, 304, 306, 308, 309, 311, 312, 314–316, 318, 323, 325–327, 333–336
1960 potential needs, 484
nutrient value, 330–337
phosphates present, 302–304
quality control, 337–340
rates of application, 419–423, 439–440
reactions with soil, 97–106
recommendations based on soil tests, 179, 180–181
requirements, by continents and countries, 462–483
by soil regions, 459–462
residual effects, 253–254, 434, 437–438
supply problems, 457–458
time of application, 439–440
usage in Great Britain, 427–447
U. S. requirements, 423–424
world, consumption, 450, 451–457
production, 451–457
requirements, 458–484
Photosynthesis, 33–37
Phytin, 13, 135–136, 154, 224
Placement of phosphorus, depth, 259, 261, 263, 264
drilled *vs.* broadcast, 258, 259, 260
in establishment of pasture, 260–261
indirect effects on crop responses, 259–260
multiple band, 259
on crops in the rotation, 257–260
on established pastures, 261–264
subsoil fertilization, 269
subsurface, 263–264
top-dressing pastures, 261–263
Plant composition, 48–49
Plant residues, effects on availability of soil phosphorus, 249–250
Potash-phosphate ash, 399
Potassium metaphosphate, 219, 220
Potassium phosphate, 223
Pyridine nucleotides, 19–20, 26–28

R

Radio-phosphorus, 10, 11, 45, 49, 56, 108, 109, 110, 165, 176, 192, 193, 213, 232–233, 244, 246, 411
Raw phosphates, availability, 195–197, 210
consumption, 193, 194
description, 194
relative efficiencies in different regions of U. S., 197–210
Refixation of phosphorus during extraction, 157–158, 160, 161, 162, 163
Residual effects of phosphorus fertilizers, 107–108, 115–118, 253–254, 434, 437–438

Residual phosphate in soils, 66–67, 107–108, 115–118
Rhenania phosphate, 222, 235, 303, 433
Rock phosphate, 55, 193–211, 234–235, 294, 350, 377–378, 396, 397
  effect on soil tests, 176–177
  production in North America, 452
  solubility, 301, 308, 335–337
Rock phosphate magnesium silicate glasses, 222, 223, 235–236, 305, 308
Root distribution in relation to placement of phosphorus, 258–259

S

Salt effect, retention of phosphate by soils, 77
Sesquioxides, effect on phosphorus dissolved, 163
Silicophosphate, 222, 235, 303, 433
Slag, calcium silicate, 399
Sodium phosphate, 223
Soil, acid, effects of lime on crop yields, 283–286
  colloids, effect on extractable phosphorus, 159–162
  moisture, effect on nutrient uptake, 101
    relation to phosphorus availability, 270–271
  solution, 2, 3
  tests, mass analyses, 177
    for phosphorus availability, 155–166
    reporting, 178–179
    use of summaries, 181–183
  virgin, phosphorus status, 402–406
Soil phosphorus, acid-soluble, 62–64, 65–66, 156–157
  adsorbed, 64, 72–73
  alkali-soluble, 64, 65, 129–131, 157
  availability, effects of carbon dioxide, 248, 250
    effects of liming, 281–296
    effects of organic materials, 247–250
    optimum pH, 284–286
    tests, 153–183
  calcium phosphate-complexes, 64
  classification, 64
  content in U. S. soils, 401–406
  distribution in profiles, 65–66, 403–405
  effects of cropping, 407–408
    of erosion, 412–413
    of farm manure, 409–411
    of fertilizers, 411–412
    of liming, 408–409
    of soluble salts, 97–99
  fertility trends, 413–419
  forms, 90, 153
  fractionation, 65
  influence of management practices, 406–413
  influence of supply, on growth, 47–48
    on phosphorus absorption, 49–50
    on plant composition, 48–49
  lattice, 66–67
  organic, 61–62, 123–144
  residual, 66–67, 107–108, 115–118
  in virgin soils, 402
  water-soluble, 62, 155–156
Solubility scales, ammonium and calcium phosphates, 300, 301
Soluble salts, effect on phosphorus uptake, 100, 101
    on residual phosphorus solubility, 98–99
    on root membranes, 100–101
Specific surface, phosphate fertilizer materials, 309, 310
Subsoil phosphorus, availability, 176, 267
  distribution, 266
  positional availability, 267–269
  utilization, 264–270
  in various horizons, 265–268
Sugars, phosphorylated, 14–16
Sulfur shortage, effect on superphosphate supply, 189, 383–385
Sulfuric acid, from sulfur or pyrites, 383
Superphosphate, 190–193, 197, 198, 199, 200, 201, 202, 203, 204–209, 213, 215, 216, 218, 219, 220, 221, 222, 223, 224, 227–232, 233–234, 244–247, 324, 433, 434, 436, 437, 438, 439, 440, 453–454
  ammoniated, 227–232, 236
  concentrated, 191, 201, 212, 216, 226, 234
  granulation, 191–193, 234, 435
  normal, 324, 325

phosphatic constituents, 324
residual effects, 253–254
solubility, 324, 325
Surface phosphate, amount in soil, 110, 115–116
measurement, 109
relationship to plant available phosphorus, 111–112
Surface sorption, by calcined phosphates, 310–312

T

Temperature, effect on phosphate retention by soil, 76
Time of phosphorus application, in advance of planting, 255
economic considerations, 254
to established postures, 256
Titanium phosphates, 60
Tricalcium phosphate, 212, 235, 311, 377
Triple superphosphate, 191, 324, 379–381, *see also* Superphosphate

U

Uranium, byproduct from phosphate manufacture, 392–393

V

Vanadium, byproduct from phosphate manufacture, 398

W

Western phosphates, 395–396

PAU CENTRAL LIBRARY
Acc: No: G 790
Date: 27.2.86

ANDHRA PRADESH AGRICULTURAL UNIVERSITY

PROF. JAYASHANKAR TELANGANA STATE
Agricultural University
University Library, Rajendranagar, Hyd-30.

Accn. No. CA790 *Call No.* 631.86
N53PIE

The book should be returned on before the last date stamped below. Otherwise fines as per the Library rules be charged.

G7790

PROF. JAYASHANKAR TELANGANA STATE
Agricultural University
University Library, Rajendranagar,
Hyderabad - 500 030.

ACC. No. G7790
Call No. 631.86 N53PIE
Author Pierre, W.H.
Title Soil Fertility and Phosphorus

PJTS Agricultural University

University Library Hyderabad - 500 030.

Accession No. G7790

1. Books may be retained up to the due date.
2. Books may be renewed on request at the discretion of the Librarian.
3. Failure of return the book in time shall render the borower to an overdue charge from the date when the book was due.
4. Dog-earing the pages of a book, marking or writing therein with ink or pencil, tearing or taking out its pages or otherwise damaging it will constitute an injury to the book.
5. Any such injury to a book is serious offence Unless the borrower points out the injury at the time of borrowing the book, he/she shall be required to replace the book or pay its price as per rules.

Help to keep the book fresh and clean.