

BIOGRAPHICAL SKETCH

The author was born on July 8, 1920 at Galle, Ceylon. His academic career began with his admission to the Ceylon University College, in July 1938, as a candidate for the B. Sc. Honours Examination of London University with Chemistry as principal subject and Physics as subsidiary subject. He received his degree in 1942 and with it the Gold Medal for Chemistry awarded by the Ceylon University College. After a period as Research Assistant in Chemistry at the University of Ceylon he joined the School of Agriculture, Peradeniya, as Lecturer in Chemistry. In July, 1950 he was appointed to the post of Acting Assistant Chemist, Department of Agriculture, Ceylon. A year later he received a United States Government Smith-Mundt grant which enabled him to come to Cornell for higher studies. He received his Master's degree in June, 1952 and proceeded as a Ceylon Government Scholar to his Doctorate with a major in Soils and minors in Field Crops and Plant Physiology.

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*NOTE: The photographic illustrations are not reproduced in this edition.

1. INTRODUCTION

The chemistry of submerged soils is a subject of unusual scientific interest and great practical utility. Its scientific interest springs from the many extraordinary features of submerged soils and the problems they present to the investigator. Its practical significance hardly needs emphasis, for rice, the most important crop in the world, is almost universally grown on submerged land.

Although rice is almost everywhere grown on submerged land and in the Orient submergence of the land has for centuries been assumed to be a sine qua non for successful rice culture, no scientific evidence had been adduced in support of this practice. It was left to American workers, in comparatively recent times, to test the validity of this practice and confirm its soundness.

Cralley and Adair (55),* in a study of irrigation treatments, found that rice plants grown on continuously submerged plots were larger, tillered better, gave significantly higher yields and a higher grain-straw ratio than plants grown on plots kept moist but not submerged. They also noted that normal irrigation was superior to intermittent irrigation, and the moist, not submerged treatment the worst. They attributed the inferiority of the moist, not submerged, plots to weed competition.

Jenkins and Jones (114), from a study over a six-year period of the effect of discontinuous versus continuous submergence, came to a similar conclusion. They found that early continuous submergence was better than intermittent drying and submergence of the land, and noted further that submergence could be delayed thirty or even forty days after seedling emergence if grasses and semi-aquatic weeds were absent.

Chambliss and Jones (44) provide further evidence of the benefits of submergence. In a study, over a three-year period, of the influence of submergence on yield, they obtained the largest yields on land that was submerged fifteen days after the rice plants had emerged. With each successive fifteen days' delay in submergence, there was a progressive reduction in yield. They ascribed the reduction in yield to weed growth. When weeds were controlled by crop rotation they were able to delay submergence thirty days after emergence with no apparent loss in yield.

Finally, Jones (123) states: "In the Orient and elsewhere even the best upland varieties give lower yields when grown on upland than under irrigation."

These investigators, while emphasizing the beneficial effects of submergence, without exception attribute them to the control of weeds.

* Figures in parenthesis refer to literature cited.

Ramiah (194), on the basis of experiments in India, expresses a similar opinion.

The only field experiment which admits of a different interpretation, though not a conclusive one, is one conducted by Jones (120) in 1923. In a report on a series of experiments "principally concerned with yield under different irrigation treatments rather than with grass control" he presents figures to show that the no submergence was markedly inferior to changing, stagnant and fluctuating water treatments. "Yields from plots kept moist, not submerged were lower than from submerged plots. Rice grown in this way stools less than that grown on submerged land, does not grow as tall, has shorter and fewer heads per plant, is not as vigorous and produces grain of inferior quality. Plenty of water for irrigation is essential for successful rice culture."

This experiment, once again, emphasizes the importance of submergence but it is by no means clear whether the complicating effect of weeds was completely eliminated. Evidence for the beneficial effects of submergence apart from the control of weeds is provided by greenhouse studies in which the confounding effect of weeds is presumably excluded.

Greenhouse studies on the comparative effects of well drained and submerged soils on the growth and yield of rice are, unfortunately, few in number and limited in character. Despite these limitations the evidence is clear that suppression of weed growth is not the only factor responsible for the better performance of rice on submerged soils than on soils kept moist but not submerged.

In a greenhouse study Vlamis and Davis (243) found that both upland and lowland rice grew better in submerged clay and loam soils than in the same soils kept moist, while barley and tomatoes did badly or failed to grow at all. They noted that submergence caused a marked increase in the growth of shoots and an even more pronounced increase in the growth of roots. But the fact that they did not continue the experiment to maturity detracts somewhat from the value of their study. This deficiency is supplied by the finding of Miura and Kaneki (164) that delaying submergence till ten days before heading markedly reduced the yield. The greenhouse experiments of Yoshino and Kawaski (256) also indicate that if submergence is unduly delayed, tillering and yield are very adversely affected. Finally, there is the finding of Chakladar (43) that even upland rice gave the highest yield in a near-saturation environment.

The evidence is clear that submergence of the soil is beneficial to rice. But, apart from the threadbare explanation that submergence helps to control weeds, not a single valid reason has been adduced by workers in the field of rice research for the necessity of this practice. Van de Goor (87) cites some advantages of the practice but they relate strictly to field conditions. Green (88) from a study of flooded organic soils in Florida also surmises some of the possible benefits of submergence of the soil in rice culture. But these are

benefits of a long term character. The only physiological explanations that have been attempted are those of Lin (147) and of Subrahmanyam and co-workers (230). Lin, on the basis of nutrient solution studies, suggested that the beneficial effect of submergence might be associated with greater availability of iron. Subrahmanyam and associates felt that it might be due to increased availability of silica. Clearly the need was indicated for the elucidation of some of the fundamental reasons for the preference of rice for a submerged milieu. A study of the chemistry of submerged soils in relation to the growth of rice suggested itself as the most fruitful approach to the problem, for it is inconceivable that so radically different a chemical environment as is present in a submerged soil cannot affect for good or ill a plant which is apparently amphibious in its habitat.

2. THE CHARACTERISTICS OF SUBMERGED SOILS

The most obvious characteristic of a submerged soil is the presence of a layer of standing water. This surplus of water has a profound effect on the soil, which manifests itself in certain well defined physical, physico-chemical, chemical and biological conditions. They are so inextricably linked one with another that the only justification for considering them separately is expediency.

2.1 Physical Characteristics of Submerged Soils

One of the immediate effects of inundation is the drastic curtailment of the normal process of gaseous exchange between soil and air. The magnitude of this effect is evident from the relative values in air and in water of the diffusion coefficient D , in the equation

$$v = - aD\left(\frac{T}{T_0}\right)^2 \frac{dp}{dl}$$

in which

$$v = \text{c.c. cm}^{-2} \text{ sec}^{-1}$$

a = porosity factor

$\frac{dp}{dl}$ = pressure gradient

T = absolute temperature.

For oxygen the ratio $D_{\text{water}}/D_{\text{air}}$ is of the order of 10^{-4} . The changes in porosity factor and pressure gradient are insignificant compared with the 10,000 fold decrease in the diffusion coefficient. Thus the entry of oxygen (and other atmospheric gases) is severely restricted. The escape of soil gases by diffusion is affected to the same degree. The net result is that the concentration of oxygen in the soil is reduced to a very low value, while that of soil gases, notably carbon dioxide, is increased, especially if conditions are favorable for biological activity. The relationship between the concentrations of oxygen and carbon dioxide need not necessarily be reciprocal but invariably the concentration of carbon dioxide is much higher than for a normal soil. The depletion of oxygen and accumulation of carbon dioxide have important consequences which will be considered in due course.

The drastic restriction of the diffusion of oxygen does not imply that the entire profile of a submerged soil is uniformly devoid of oxygen. The concentration of oxygen can be relatively high at the

surface and again at some depth below. Sandwiched between these is a layer of soil which may be practically devoid of oxygen.

The evidence for the presence of a relatively high concentration of oxygen in a thin layer of soil immediately below the surface comes from the brilliant researches of Pearsall (178, 179, 180, 181) and Mortimer (166, 167), jointly and individually, on lake muds and sediments and swamp soils. Pearsall and Mortimer showed that in lake muds in contact with aerated water there was a thin layer at the surface, varying in thickness from a few millimeters to a centimeter, which could be differentiated from the mud below it by differences in color, chemical and physico-chemical properties, and biological activity. Chemically this layer was characterized by the presence of oxygen and typical oxidized radicals, such as ferric iron, nitrates and sulphates, while the mud below was low in oxygen and contained ferrous iron, nitrites, ammonia and sulfides. Redox potentials were in line with these observations. Mortimer's (167) figures show that the oxygen concentration dropped sharply in the first centimeter from the surface and was reduced to zero at a depth of four centimeters. The redox potential (E_7) dropped from +0.50 volt at the surface to -0.10 volt at a depth of 4 cm.

Mortimer (167) has suggested that a dynamic balance is attained between the diffusion of oxygen into the mud and its consumption by the mud and that the thickness of the oxidized layer is a measure of it.

There is evidence also for the presence of a zone of relatively high oxygen concentration at some depth in submerged soils. Direct proof of this is furnished by Furr and Aldrich (82). They found that after irrigation the oxygen content at a depth of 96" remained continuously at 15-17 percent although at 6" it fell from 20 to 5 percent. There is indirect evidence for the presence of such a zone in paddy soils which are kept flooded and dry in alternate seasons. DeGee (66) has shown that the redox potential of a typical paddy soil is high at the surface, drops suddenly to a low value at a depth of about a centimeter and resumes a high value in the subsoil. Shiori and Tanada (213) confirm this. These observations taken in conjunction with Koenig's (138) explanation of the formation of a compact layer of manganese dioxide and oxidized iron in the plow pan of paddy soils suggest a high oxygen concentration in the subsoils of paddy fields. But the zone of root development in a submerged soil is practically devoid of oxygen.

The depletion of oxygen is accompanied and followed by an increase in the concentration of the typical gaseous products of the anaerobic decomposition of organic matter, such as methane and hydrogen. Harrison and Aiyer's (93) analyses of the gas escaping as bubbles from the surface of flooded rice soils in India illustrate dramatically the nature and the extent of the change in gas composition caused by submergence. The gas was found to consist mainly of methane and nitrogen.

The relative proportion of these gases varied greatly, the methane from 15 to 75 percent of the total, and nitrogen from about 10 to 95 percent. Carbon dioxide was generally present together with small amounts of oxygen and hydrogen. The proportion of carbon dioxide varied from 1 to as high as 20 percent, with an average of about 5 percent. Oxygen was present only in traces. Hydrogen was generally absent but in certain uncropped soils it was as high as 10 percent.

Less conspicuous among the physical effects of flooding are changes in mechanical properties, structure, permeability and temperature.

Sturgis (227) emphasizes the deleterious effects of flooding on soil structure and cites evidence in support of his contention that deflocculation of the soil is the cause of the low productivity of certain Louisiana soils long under rice cultivation. It is not clear, however, whether flooding per se, or the accumulation of alkaline substances from the irrigation water, is the cause of this. On the other hand it has been suggested that one of the beneficial effects of a rice crop preceding sugar cane is the improvement in structure brought about by the cementing action of oxidized iron. In sharp contrast to Sturgis, Van de Goor (87) affirms "flooded conditions prevent deterioration of structure."

Of the permeability studies on submerged soils, that of Allison (9) deserves special mention. Allison found that the permeability of a continuously submerged soil decreased at first and then increased as the entrapped air was removed by solution. Subsequently a marked decrease in permeability occurred. He attributed this to the clogging of the soil pores by products of bacterial metabolism and advanced the view that the sealing of the pores contributed towards water economy in rice culture.

Submergence affects mechanical properties such as cohesion, plasticity and consistency. The only significant change in so far as the growth of the rice plant is concerned, is perhaps the removal of some of the mechanical obstructions that are sometimes encountered in dry soils.

The effect of submergence on soil temperature follows from two important thermal properties of water, namely, its high specific heat and high heat of vaporization. The high specific heat prevents violent fluctuations in the temperature of flooded soils. The high heat of evaporation tends to keep flooded soils cooler than dry soils. The cooling effect of flooding is utilized in reducing high temperature injury in hot locations (220) while the stabilizing effect of water on soil temperature is used to prevent low temperature injury at night (206).

2.2 Physico-chemical Characteristics of Submerged Soils

Submergence of a soil brings about a number of physico-chemical changes. Important among them are an increase in pH, an increase in specific conductance, and a decrease in redox potential.

2.21 Increase in pH

Submergence of a soil leads to a gradual increase in pH. The magnitude of the change appears to depend on the initial pH, the organic matter content and duration of submergence.

Among the earliest references to the effect of submergence on the acidity of a soil are those of Connor and Gillespie. As far back as 1918, Connor (51) found that acidity of soils kept at different moisture contents was markedly affected by the moisture content. The changes in acidity were accompanied by changes in the concentration of several constituents, notably iron and manganese. But his terminology is so obscure that the task of interpreting his results is left to the reader. His data clearly show that there was a marked decrease in acidity with increase in moisture content. This decrease in acidity was associated with an increase in the concentration of iron and manganese.

Gillespie (85) noted a decrease in hydrogen ion concentration when a soil was submerged, but wondered whether it was real or a result of the poisoning of the platinum electrode used for its measurement. It was left to Subrahmanyam (228), seven years later, to demonstrate the reality of the decrease in hydrogen ion concentration. Subrahmanyam observed an increase in pH some days after the submergence of certain temperate and tropical soils. Since there was a concomitant increase in ammonia he attributed the increase in pH to this. But Schollenberger (209), a year later, showed that a moist soil kept under anaerobic conditions increased in pH value although there was no increase in ammonia. He demonstrated very clearly that an increase in the concentration of manganese is certainly one of the causes of the increase in pH.

The earliest field study was that of Dennett (67). Dennett observed a marked difference between the pH values of paddy soils in the dry and in the flooded states. Typical changes were pH 4.5 - 5.0 in the dry state, to pH 6.5 - 7.0 in the flooded condition. The changes were reversed on letting the soil dry out. He was the first to draw attention to the role of the Fe^{+++} - Fe^{++} equilibrium in affecting the pH values of soils. Joffe (118) two years later assigned the same role to iron when he drew attention to the reversible pH changes in the glei horizons of poorly drained soils.

The findings of Reed and Sturgis (199) are interesting because they reveal a connection between initial pH and the magnitude of the increase.

Initial pH	pH 18 weeks after submergence
5.00	6.55
6.45	7.27

The increase is clearly more pronounced at the lower pH. Their data also indicate that in the presence of organic matter the pH increase was greater. Karunkar and Daniel (130) confirm this.

The evidence for the increase in pH of the soil on submergence is incontrovertible but the physico-chemical causes underlying this change are not clearly understood. Subrahmanyam (228) and Metzger (155) have attributed it to ammonia, and Karunkar and Daniel (130) have even attempted to correlate pH fluctuations in a flooded rice soil with variations in the ammonia concentration. Dennett (67) and Joffe (118) have emphasized the role of ferrous iron, while Schollenberger (209) cited evidence for the part played by reduced manganese in this change. Mortimer (166) found that the increase in alkalinity of lake muds, following thermal stratification and depletion of oxygen, could be accounted for by the increase in iron, manganese and ammonia, but in a tank study of a lake mud he noted that ammonia alone was sufficient to account for the increase in pH, despite the production of ferrous and manganous compounds.

Ammonia, manganous hydroxide, and ferrous hydroxide are all weak bases which can neutralize the hydrogen ions of the soil colloids, but direct proof of this reaction has been given only for manganese. Aside from Schollenberger's (209) experiment, there is evidence for the alkaline effect of reduced manganese from the behavior of the quinhydrone electrode when used in the determination of pH of manganiferous soils (168).

The increase in pH is all the more remarkable when it is realized that this occurs in spite of a several hundredfold increase in carbon dioxide concentration and a noticeable increase in total salt content as judged by specific conductivity measurements. Both these factors tend to lower the pH.

The physico-chemical principles underlying the calcium-carbon dioxide - pH equilibrium have been clearly expounded by Bradfield (32). It follows from them that a high carbon dioxide concentration can have a marked depressing effect on the pH of a soil even in the presence of excess calcium carbonate. This is due to the hydrogen ion concentration increasing more rapidly than the calcium ion concentration with increase in the partial pressure of carbon dioxide. The presence of ferrous and manganous compounds and ammonia in submerged soils renders a direct application of these principles to them impracticable but the restraining influence of carbon dioxide on pH increases is indicated.

2.22 Specific Conductance

Submergence of a soil leads to the production of a large amount of soluble matter. This was first clearly demonstrated by Connor (51), and confirmed by numerous subsequent researches. This increase in concentration of soluble matter should manifest itself in a rise in specific conductance. Unfortunately, studies on the specific conductances of typical submerged soils are practically nonexistent. Here, as in numerous other places, the researches of limnologists prove useful.

Mortimer (166) reports that one of the striking consequences of the establishment of thermal stratification, with its consequent depletion of oxygen in the hypolimnion of a lake, is an increase in electrical conductivity of the water near the surface of the mud. He attributed the increase to the increase in concentration of iron, manganese, ammonia and other bases liberated from the reduced mud. In tank studies he confirmed his outdoor observations and stressed the necessity of anaerobic conditions for the increase in conductivity of the water in contact with the mud. He further noted that after a steady increase for 117 days the conductivity began to decline. He attributed this to the precipitation of ferrous sulfide.

While an increase in specific conductance as a consequence of submergence is theoretically possible and practically demonstrable, the relationship between soluble salt content and conductance is obscure. The various empirical relationships (136, 200, 246) that have been derived for upland soils, in which the ions are Cl^- , SO_4^{--} , NO_3^- , HCO_3^- , Na^+ , K^+ , Ca^{++} , and Mg^{++} , are clearly not applicable to these soils in which the chief soluble components are probably bicarbonates and organic salts of iron, manganese and ammonia.

The increase in conductance is remarkable because submergence leads to a disappearance of NO_3^- , as a result of denitrification, and of SO_4^{--} , as a result of reduction and removal of sparingly soluble sulphides. There is, however, the compensating effect of increased carbon dioxide concentration the influence of which on the specific conductance of soils with an excess of calcium has been stressed by Bradfield (32). This effect of carbon dioxide is confirmed by a reference to the equation

$$\text{pH} = \text{pK}_1 + \log \frac{(\text{H CO}_3^-)}{(\text{H}_2 \text{ CO}_3)}$$

The several hundredfold increase in carbon dioxide concentration (93) observed in submerged soils would lead to an appreciable increase in the bicarbonate ion concentration, especially at high pH values.

2.23 Redox Potential

The single physico-chemical property that serves to differentiate a well drained soil from a submerged soil is its redox potential. The oxidized state of a well drained soil is reflected in its high oxidation-reduction or redox potential* while the reducing condition that usually prevails in a submerged soil manifests itself through a low redox potential. The practical value of the measurement of redox potentials is attested by the very large number of studies on the redox potentials of soils, lake muds and waters, bacterial cultures, and sewage, and is summarized by Pearsall and Mortimer (181) in these words:

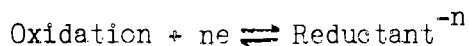
* Redox potential and oxidation-reduction potential will be used interchangeably in this thesis.

"In the measurement of potential we have a method of showing whether a soil or a natural system is capable of oxidation or otherwise, under conditions where direct oxygen measurements are inconvenient or impracticable. Further, in many cases it is probable that the oxidation-reduction potential, i.e., the value which indicates the general level of oxidation or reduction of a system, is a factor of greater biological significance than oxygen concentration alone."

In this review it is proposed to consider redox potential under three heads: (a) theory; (b) redox systems in soils; and (c) factors that influence the redox potentials of soils.

(a) Theory.

Oxidation is a process in which a substance, atom, or radical, loses electrons; reduction is its reverse. It is clear at once that oxidation-reduction is a conjugate process, the electron donor undergoing oxidation, and the acceptor reduction. The oxidation-reduction or redox potential is a quantitative measure of the level of oxidation-reduction of the system, and is given by the electrical potential which an inert electrode, such as platinum or gold, assumes in contact with the system. It can be shown thermodynamically that for a system of the type,



the redox potential is given by the expression

$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Oxidant})}{(\text{Reductant})}$$

where E_h is the potential relative to the normal hydrogen electrode taken as zero, E_o is a characteristic of the system and equal to E_h when the ratio (Oxidant)/(Reductant) is unity, and the other symbols have the customary significance.

It is clear at once that redox potential in any given system is determined by the ratio of oxidant to reductant and is therefore a measure of the intensity of oxidation or reduction.

When two redox systems are mixed a redistribution of electrons takes place among the components (if energy barriers are absent) which brings the potentials of the two systems to a common value. This final potential is determined by the system which is present in excess. This is very clearly illustrated by the numerical example Michaelis (157) has given of the interaction between the ferric-ferrous system and the methylene blue-leuco methylene blue system. His figures show that if the ferric-ferrous system is present in excess practically all the leuco-methylene blue is oxidized without a marked deviation from the potential of the ferric-ferrous system. If, on the other hand, leuco-methylene-blue is present in excess of Fe^{+3} practically all the Fe^{+3} may be reduced

without appreciably changing the potential of the methylene-blue-leuco methylene blue system. This is a point of great significance in interpreting redox potentials of the mixed systems that are present in soils.

A property of equal importance, especially in the measurement of redox potentials of soils, is the resistance to change or "poise" of a redox system. Lack of poise is the cause of the electrode drifts, the electrode lags and the failure to get reproducible readings so often described in the literature.

An expression for the poise of a system can be derived mathematically from the equation for the redox potential of a system.

$$E = E_O + \frac{RT}{nF} \ln \frac{x}{A-x}$$

in which x = activity of oxidant

A = activity of (oxidant + reductant)

The increase in potential with a small increase in the concentration (activity) of the oxidized phase is given by

$$\frac{dE}{dx} = \frac{RT}{nF} \cdot \frac{A}{x(A-x)}$$

The reciprocal of $\frac{dE}{dx}$ may be taken as a measure of the poise of the system and is given by the expression

$$\frac{nF}{RT} \cdot \frac{x(A-x)}{A}$$

On differentiating this with respect to x it is apparent that poise is maximum when

$$x = \frac{A}{2} ;$$

that is, when oxidant and reductant are present in equal concentration. It can be shown further that the poise increases with the total concentration of oxidized and reduced states.

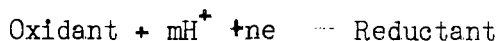
The poor poise of well aerated soils is due to the absence of a reversible system in sufficiently high concentration. Oxygen is present at a high concentration but it does not function reversibly at the blank platinum electrode used for the determination of redox potentials of soils. The better poise of submerged soils (224) may be attributed to the high concentration of reduced products and to the presence of systems whose standard oxidation-reduction potentials are of the order of the potentials of submerged soils.

In the simple system used as an example in the preceding section, the concentrations of oxidant and reductant were assumed to be independent of certain factors that often influence redox potentials. Of these factors, complex ion formation and changes in hydrogen ion concentration are the most important.

Complex ion formation can have a marked effect on the redox potential of a system by inactivating a part of the oxidized or reduced phase. A striking example is the effect of sodium fluoride on the $\text{Fe}^{+3} - \text{Fe}^{+2}$ system. The addition of sodium fluoride to the $\text{Fe}^{+3} - \text{Fe}^{+2}$ system can, according to Michaelis (157), cause a potential drop from 0.74 volt to 0.0 volt owing to the removal of Fe^{+3} as the complex ion FeF_6^{-3} . Another example of the influence of complex ion formation on potentials may be found in Kohnke's (139) observations on the behaviour of the $\text{Fe}^{+3} - \text{Fe}^{+2}$ system in the presence of certain organic acids. Since both iron and manganese have a strong tendency to form chelated complexes with certain components of soil organic matter, it may be concluded that the pure iron and manganese systems undergo considerable modification in the soil.

Changes in hydrogen ion concentration can affect redox systems directly by the participation of hydrogen ions in the oxidation-reduction, or indirectly, by influencing ionic equilibria.

There are numerous examples of the direct participation of the H^+ ion in oxidation-reduction but its action may be illustrated by a general example:



The expression for the electrode potential becomes

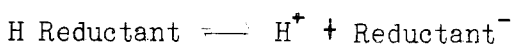
$$E_h = E_o + \frac{RT}{nF} \ln \frac{(\text{Oxidant})(\text{H}^+)^m}{(\text{Reductant})}$$

or

$$E_h = E_o + .058 \log \frac{(\text{Oxidant})}{(\text{Reductant})} - .058 \text{ mpH}$$

The potential of the system is influenced by pH and the $E_h - \text{pH}$ slope is $-.058\text{m}$.

The H^+ ion concentration can affect the redox potential of a system by influencing the ionization of one of its components. For a simple system in which the oxidized form is un-ionized and the reduced form is a univalent anion the following equilibria will hold:



For this system it can be shown that

$$E_h = E_o + \frac{RT}{F} \ln \frac{(\text{Oxidant})}{(\text{Reductant})} + \frac{\text{H}^+ + K_a}{K_a}$$

in which H^+ is the activity of the hydrogen ions and K_a , the dissociation constant of the un-ionized form of the reductant. If the ratio of oxidant to reductant is kept constant, the potential of the system is determined by the term $\ln (H^+ + K_a)$.

$\frac{dE}{dpH}$ thus depends on the relative values of H^+ and K_a .

At 30°C $\frac{dE}{dpH}$, i.e., the slope of the E_h - pH curve, can vary

from 0 to - 60 millivolts per unit change in pH, the actual slope depending on the pH of the system. Clark (50) has derived expressions for dE/dpH for more complicated systems where polyvalent anions or polyvalent cations are involved. If both the oxidized and reduced forms are ionized to form polyvalent ions, the E_h -pH relationship becomes extremely complicated.

In the case of soils the relationship may be still more complicated, owing to the presence of mixed organic and inorganic systems, so that it is impossible to formulate a general rule as to the effect of pH on redox potential. It is a matter of great surprise, therefore, to find so many workers in the field of soil science referring to "the theoretical slope" of 60 millivolts per pH unit for soil systems. Peech and Batjer (183), however, summed up the complexity of the E_h - pH relationship in these words:

"Changes in hydrogen ion concentration may alter the ratio of oxidant to reductant by inducing oxidation, chemical precipitation and complex ion formation, so that the ultimate effect of the hydrogen ions may be very complicated indeed. It is surprising to see as good an E_h -pH relationship as one finds in different soils."

The variability of the values given in the literature for the E_h -pH slopes of soils emphasizes the complexities of the relationship as predicted by theory. The figures of Willis (249) for the changes in redox potentials of a soil caused by liming indicate a slope of 67.* Heintze (100) found that the E_h -pH curve was a straight line parallel to the E_h -pH line for the quinhydrone electrode, and concluded that there was a redox system similar to the quinhydrone system, in soils. Bradfield and co-workers (33) obtained an average value of 80 for many well drained and water logged New York soils. Darnell and Eisenmenger (57) found that the slope varied from 38-59 with a mean of 54. Buehrer, Martin and Parks (41) reported that the figure varied from 53-100 when the pH changes were brought about by the addition of acid or alkali, but when the pH was increased by merely diluting the system the slope was 68. Puri and Sarup (190) obtained values ranging from 27-76, with a mean of 53, for fifty-eight Indian soils tested; yet, they made the surprising statement, "The relation between pH and E_h is so perfect that the measurement of pH should suffice for all practical purposes."

* i.e., -67 millivolts per pH unit.

Although some investigators have been impressed by the regularity of the E_h -pH relationship under the conditions of their limited studies it is clear, from the wide range of values obtained for the E_h -pH slope, that any approximation to the theoretical value for the hydrogen electrode may be purely fortuitous. This emphasizes the necessity of determining the E_h -pH relationship for each soil in the study of redox potentials.

The variation of the redox potentials of certain systems with pH has a consequence of great significance in the interpretation of oxidation-reduction phenomena in soils -- it can alter drastically the relative position of a system on the redox scale with the oxygen and hydrogen systems at the extremes. For example, the standard oxidation-reduction potentials for the systems $MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{+2} + 2H_2O$ and $NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2OH^-$ are 1.23 volt and 0.0 volt respectively. This would imply that the reduction of nitrate to nitrite occurs only after considerable amounts of MnO_2 are reduced. On conversion to pH 7.0, however, the standard oxidation-reduction potentials become 0.43 volt for the MnO_2 - Mn^{+2} system and 0.41 volt for the NO_3^- - NO_2^- system. On this basis reduction of MnO_2 and NO_3^- should proceed almost simultaneously at pH 7.0.

The effect of pH on the relative position of the iron system on the redox scale is even more striking. The standard electrode potential for the $Fe^{+3} - Fe^{+2}$ system is 0.77 volt. Theoretically, therefore, Fe^{+3} should be reduced long before the potential has dropped low enough to cause an appreciable reduction of NO_3^- . There is evidence (178, 167, 254), however, that Fe^{+2} does not appear in appreciable amounts in anaerobic soils until NO_3^- has disappeared almost completely. The anomaly disappears when the standard potentials corrected to pH 7.0 are compared. They are 0.41 volt for the NO_3^- - NO_2^- system and -0.10 volt for the $Fe^{+3} - Fe^{+2}$ system.

(b) The redox systems in soils

The potentials that have been obtained with soils cover almost the entire range between the oxygen and the hydrogen systems. In this range there are several inorganic systems which may be applicable to soils. The difficulty arises when it comes to identifying the organic systems that undoubtedly operate in soils. Soil organic matter is such a heterogeneous mass of organic substances in all stages of decomposition together with microbial cells and their metabolic products, that the identification of the organic systems in soils is almost a hopeless task. The problem is further complicated by the fact that many biological oxidations are irreversible and do not give thermodynamic potentials. There is, however, an indirect approach to the problem.

Of the metabolic processes that go on in the soil, respiration is the most important. Besides, it is a typical oxidation-reduction. It is not unreasonable, therefore, to suppose that some of the systems involved in respiration contribute towards the redox system in soils. It may be objected that these systems operate only within the cells.

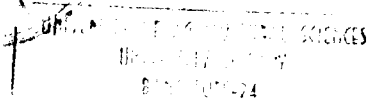
But there is abundant evidence (50, 104, 157, 224) that bacteria influence the potential of the medium in which they function. The next problem is the mechanism involved. Yudkin (259) poses the problem in these words: "The main problem was to decide whether the potentials were being caused by contact with the electrode of the bacteria, possibly with adsorbed reactants or by contact with the electrodes of the reactants themselves moving freely in the solution." He noted that bacteria-free solutions obtained by using collodion sacs gave as low a potential as in the presence of bacteria and provided the solution to his problem as follows: "It seems fairly certain from the results given that the reduction potential of a bacterial suspension as measured at an electrode is produced by substances in solution in the suspension. The potentials recorded in the absence of substrates are probably due to substances exuded by bacterial cells." It is clear, therefore, that substances produced in bacterial cells can diffuse out and influence the potential, but it must be emphasized, as Yudkin did, that the potential measured need not be the potential inside the cell. Yudkin's findings indicate that some of the products of respiration diffuse out of the cells and may influence the redox potentials of soils, but whether these substances will function as redox systems, as they do inside the cells, will be determined by the presence or absence of the appropriate enzymes in the medium. Unfortunately, this is a question to which there is no satisfactory answer at the present time.

Assuming that some of the redox systems involved in respiration operate in soils, the following scheme can be given for the redox systems in soils:

Electrochemical reaction	E_0 Volts	E_0 at pH 7.0 Volts
$O_2 + 4 H^+ + 4e \rightleftharpoons 2H_2O$	1.23	0.82
$Fe^{+3} + e \rightleftharpoons Fe^{+2}$	0.77	
$MnO_2 + 4H^+ + 2e \rightleftharpoons Mn^{+2} + 2H_2O$	1.23	0.43
$NO_3^- + H_2O + 2e \rightleftharpoons NO_2^- + 2 OH^-$	0.0*	0.41
$Fumarate + 2H^+ + 2e \rightleftharpoons Succinate$		-0.03
$Oxalacetate + 2H^+ + 2e \rightleftharpoons Malate$		-0.10
$Fe(OH)_3 + e \rightleftharpoons Fe^{+2} + 3OH^-$	0.77	-0.10
$Pyruvate + 2H^+ + 2e \rightleftharpoons Lactate$		-0.18

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* $E_0 = .82$ at pH 0.0



Electrochemical reaction	E_0 Volts	E_0 at pH 7.0 Volts
Acetaldehyde + $2H^+$ + $2e \rightleftharpoons$ Alcohol		-0.19
$SO_3'^{\prime} + 3H_2O + 6e \rightleftharpoons S'' + 6OH'$	-0.61	-0.20
$2 H^+ + 2e \rightleftharpoons H_2$	0.00	-0.414
$SO_4'^{\prime} + H_2O + 2e \rightleftharpoons SO_3'^{\prime} + 2OH'$	-0.90	-0.49

In this list the oxygen potential represents the highest level of oxidation while the hydrogen potential indicates the highest level of reduction. It is theoretically possible for any system in the list to oxidize those below it. Since energy barriers that prevent some of these reactions in vitro are probably largely eliminated by the catalytic effects of enzymes and colloidal matter, it would appear that reduction processes in a submerged soil proceed in this thermodynamic sequence.

It is clear from the table that the systems likely to operate in a well drained, aerated soil at pH 7 are those whose potentials at pH 7.0 are more positive than the fumarate-succinate system. Of these, oxygen clearly is the most important.

In a well drained soil there is an unlimited supply of oxygen at a fairly high partial pressure. The oxygen system would, therefore, tend to dominate the potential. But the potentials of well drained soils as measured with blank platinum electrodes deviate markedly from the values predicted by theory for the oxygen system at the oxygen tensions found in well drained soils. Cooper (54) has attempted to explain this anomaly by assuming that the blank platinum electrode, normally used for the determination of redox potentials, functions as an irreversible oxygen electrode owing to the formation of an oxide film. Pearsall and Mortimer (181) have extrapolated some of Cooper's data and obtained values of the order encountered in aerated soils. They concluded: "It appears evident that potentials of surface waters of lakes, and indeed of all natural waters with a high oxygen content, are largely governed by the irreversible oxygen system."

The iron system would appear to come next in importance and, indeed, Bradfield and co-workers (32) have suggested that it is the principal system in soils. Among the reasons that have been adduced for the importance of the iron system in soils are: (i) the abundance of iron compounds in soils; (ii) the increase in concentration of ferrous iron when soils are waterlogged; (iii) the similarity of behavior of sulfuric acid extracts of soils to that of the Fe^{+3} - Fe^{+2} system when titrated potentiometrically; and (iv) soil potentials lie within the iron system. The difficulty in the way of accepting the iron system as the dominant

system in aerated soils is that its concentration is so low that it would be swamped by the more powerful oxygen system. Theoretical proof of this is provided by a consideration of the effect of pH and oxygen tension on the iron system.

The expression for the electrode potential of the $\text{Fe}^{+3}\text{-Fe}^{+2}$ system is

$$E_h = E_o + \frac{RT}{F} \ln \frac{(\text{Fe}^{+3})}{(\text{Fe}^{+2})}$$

This expression contains no term for H^+ ion concentration so it is generally believed that the potential of the iron system is independent of pH. This, indeed, is the case till a pH of 1.53 is reached from the acid side. At this pH, according to Eriksson (75), $\text{Fe}(\text{OH})_3$ begins to precipitate out. Arden (16) gives a pH of 2.5-3.5 as the pH zone in which precipitation of ferric hydroxide commences. Whatever the actual pH, it is clear that from the point of precipitation of $\text{Fe}(\text{OH})_3$, the OH^- concentration is going to determine the concentration of Fe^{+3} and, therefore, the redox potential of the system. The equation then becomes

$$E_h = E_o + \frac{RT}{F} \ln \frac{(\text{H}^+)^3}{(\text{Fe}^{+2})} \cdot \frac{K_s}{K_w^3}$$

in which K_s is the solubility product of $\text{Fe}(\text{OH})_3$ and K_w the ionization constant of water. When the numerical values of the constants are substituted, the equation becomes

$$E_h = 0.77 + .058 \log \frac{1}{(\text{Fe}^{+2})} + .058 (6-3 \text{ pH}).$$

Two important conclusions follow from this expression. First, the standard oxidation-reduction potential, corrected to pH 7.0, becomes -0.10 instead of 0.77, and secondly, the $\text{Fe}^{+3}\text{-Fe}^{+2}$ system will have an E_h -pH slope of 174 so long as the concentration of Fe^{+2} is unaffected by pH or oxygen tension. This means that in the absence of oxygen the potential will be given by the new equation till the point of precipitation of ferrous hydroxide is reached. According to Arden (16), Fe^{+2} is precipitated as "ferroso ferric" hydroxide at a pH of 6.4 in the total absence of oxygen. It may, therefore, be concluded that in the absence of air the potential of the $\text{Fe}^{+3}\text{-Fe}^{+2}$ system, at least in the pH range 3.5 to 6.4, is given by the last equation. It is remarkable that Kohnke (139) twenty years ago found that for the $\text{Fe}^{+3}\text{-Fe}^{+2}$ system in nitrogen "up to about pH 2.5 E_h varies only slightly with pH while from pH 3.5 to pH 6.8 the change of E_h per unit change of pH value is approximately .174 volts."

The presence of oxygen introduces an additional complication in that it can affect the Fe^{+2} concentration before the OH^- affects the concentration of Fe^{+2} . From the theory of mixed systems it follows that if the iron and oxygen systems are in equilibrium they will have a common potential. Thus

$$0.77 + \frac{RT}{F} \ln \frac{(H^+)^3}{(Fe^{+2})} \cdot \frac{K_s}{K_w} = 1.23 + \frac{RT}{4F} \ln (H^+)^4 (O_2)$$

$$\text{or } 0.46 = \frac{RT}{F} \frac{(H^+)^2}{(Fe^{+2})} (O_2)^{-1/4} \cdot \frac{K_s}{K_w}$$

$$\text{or } pFe^{+2} = 2pH + 1.93 - 1/4 pO_2$$

where pFe^{+2} and pO_2 stand for the negative logarithms of the Fe^{+2} concentration and partial pressure of oxygen respectively.

It may be concluded from this discussion that the potential of an iron system at pH values greater than 2.5 is determined by the partial pressure of oxygen and the H^+ ion concentration. In other words, in a well aerated soil the iron system is displaced by the oxygen system.

With the exclusion of the iron system, one is left with the $MnO_2 - Mn^{++}$ and $NO_3^- - NO_2^-$ systems as the alternatives to the oxygen system in well drained soils.

The $MnO_2 - Mn^{++}$ system has certain claims to importance. They are the widespread occurrence of the components of this system in soils, the greater solubility of Mn^{++} than Fe^{+3} and Fe^{+2} , and, lastly, the closeness of the standard oxidation-reduction potential of this system at pH 7.0 to the potentials observed in well drained soils at this pH. The difficulty is that, like Fe^{+2} , Mn^{++} is readily oxidized by atmospheric oxygen so that the concentration of Mn^{++} is determined by the oxygen tension and pH. Since the oxidation of Mn^{++} (in concentrations as low as 27 parts per million of the soil solution) by atmospheric oxygen can occur, according to Hemstock and Low (102), at a pH as low as 2.7, it may be inferred that the $MnO_2 - Mn^{++}$ system, like the $Fe^{+3} - Fe^{+2}$ system, is swamped by the oxygen system in well aerated soils.

At practically the same level on the oxidation-reduction scale as $MnO_2 - Mn^{++}$ is the $NO_3^- - NO_2^-$ system. The potentials of the system fall well within the range of soil potentials. Besides, this is a system whose concentration in the soil solution is normally high. There are strong *prima facie* reasons, therefore, for supposing that the $NO_3^- - NO_2^-$ system operates in soils. But there is one serious drawback: the $NO_3^- - NO_2^-$ system is not thermodynamically reversible *in vitro*. Presumably for this reason, the $NO_3^- - NO_2^-$ system has received scant attention in the study of redox potentials of soils. The possibility cannot, however, be excluded that, under the catalytic influence of enzymes, microbial cells, and colloidal matter present in soils, some of the energy barriers which preclude reversibility *in vitro* may be eliminated, and the system functions reversibly. If this were true, the $NO_3^- - NO_2^-$ system should have a marked influence on the potentials of redox systems. That this, indeed, is the case is shown by a number of observations reported in the literature. They relate to the stabilizing effect of nitrate on the potentials of redox systems in the vicinity of the standard potential of the $NO_3^- - NO_2^-$ system. These observations are summarized below.

Pearsall (178), in the course of a study of a wide range of soils under natural vegetation, noted that soils containing nitrate had potentials exceeding 350 millivolts at pH 5. Mortimer (166, 167) in his studies on lake waters found that a rapid reduction of nitrate occurred in the hypolimnion when the redox potential fell below 0.4 volt at pH 7. He also noted the presence of nitrite and inferred from its distribution with depth that it came from nitrate reduction. He confirmed these observations in a tank study of lake mud and gave 0.45 volt at pH 7 as the potential at which active nitrate reduction began and 0.35 volt as the level at which both nitrate and nitrite were not detectable.

It is also interesting to note that Aoki (15) noted a rise in potential on the addition of nitrate to a reduced soil.

Similar results are reported by sewage investigators. Fales (77), as far back as 1929, reported that during periods of low stream flow and warm weather the addition of sodium nitrate to the river prevented the anaerobic decomposition of paper mill and tannery effluents, with the accompanying offensive odors. Sanborn (205) found that the addition of sufficient sodium nitrate gave complete protection against odors in the treatment of cannery wastes in lagoons. Heukelekian (103) noted that sodium nitrate retarded sulphide formation in sewage and ascribed it to the preferential reduction of nitrate rather than sulfate. Finally, there is Moore's (165) observation that in a sewage solution containing 135 p.p.m. NaNO_3 E_h dropped from +.3 volt gradually to +.1 and remained at this level, while without nitrate the potential dropped to -0.1 volt in six hours.

Whatever the mechanism, the evidence is clear that the presence of nitrate (i) retards reduction, and (ii) stabilizes the potential at 200-400 mv. at pH 7. The obvious explanation is that a nitrate-nitrite system functions as a redox system.

The close of the discussion of the nitrate system provides an apt beginning for the consideration of the redox systems on the negative side of the scale.

A glance at the list of redox systems on pages 15-16 will reveal a big gap between the oxidized systems terminated by nitrate, on the one hand, and the reduced systems, as judged by the standard oxidation-reduction potentials at pH 7, on the other. It can be predicted theoretically, therefore, that the disappearance of nitrate will be followed by the onset of typical reducing conditions. Striking verification of this comes from the researches of Pearsall and of Mortimer on swamp soils, lake muds and lake waters.

Pearsall (178) concluded his first report on the investigation of the soil complex in relation to plant communities in the following words:

"We conclude from the facts summarized here that the soils examined undergo an alteration in properties

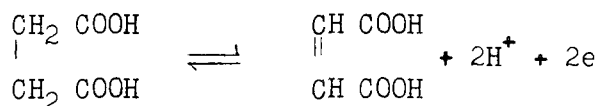
in the vicinity of E_5 320-350 millivolts, such that below that point products of reduction are demonstrable while above it oxidation products are more prominent. If these characteristics are of general application it seems that soils below E_5 320 should be regarded as effectively reducing while those above E_5 350 are predominantly oxidizing."

After further intensive studies, Pearsall and Mortimer (181) amplified and confirmed the earlier statement:

"In all cases so far examined, in soils, waters and muds representing a variety of natural conditions, products of oxidation (Fe^{+3} , NO_3^- , SO_4^{+4}) are found above the potential zone $E_5 + 350$ mv; below this zone their reduced counterparts are present."

The disappearance of nitrate marks the transition from oxidizing to reducing systems. Since nitrate does not persist in submerged soils it is reasonable to suppose that the dominant systems in submerged soils are the reducing ones.

The fumarate-malate system, the first in the reducing series, is a component of the tricarboxylic acid cycle involved in aerobic respiration. In aerobic respiration the H^+ ions and electrons removed from succinic acid by succinic dehydrogenase according to the equation



are brought into union with atmospheric oxygen through the mediation of hydrogen carriers. Under anaerobic conditions substances other than atmospheric oxygen may act as the terminal hydrogen acceptor. The evidence seems to indicate that nitrate may function as the terminal hydrogen acceptor. But with the depletion of nitrate the low potential of the system is likely to assert itself.

The oxalacetate - malate system occurs widely in biological systems and, like fumarate-malate, is a component of the Krebs cycle. Although this system, like its analogue, probably supplies active hydrogen, its contribution to the redox system in soil cannot be appreciable because of the poor poise of the system. The lack of poise is due to the extreme sensitivity of the enzyme which brings about the change to the slightest accumulation of the reaction product, oxalacetate (28).

Of the organic systems in soils, the most important are probably the two typical anaerobic systems, pyruvate-lactate and acetaldehyde-alcohol. Under aerobic conditions the reduced DPN* formed during glycolysis is reoxidized by atmospheric oxygen through the mediation of

* Diphosphopyridine nucleotide.

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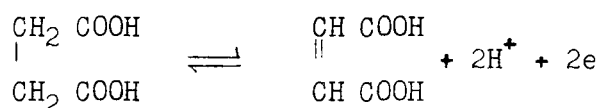
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The disappearance of nitrate marks the transition from oxidizing to reducing systems. Since nitrate does not persist in submerged soils it is reasonable to suppose that the dominant systems in submerged soils are the reducing ones.

The fumarate-malate system, the first in the reducing series, is a component of the tricarboxylic acid cycle involved in aerobic respiration. In aerobic respiration the H^+ ions and electrons removed from succinic acid by succinic dehydrogenase according to the equation



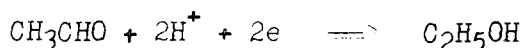
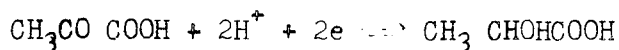
are brought into union with atmospheric oxygen through the mediation of hydrogen carriers. Under anaerobic conditions substances other than atmospheric oxygen may act as the terminal hydrogen acceptor. The evidence seems to indicate that nitrate may function as the terminal hydrogen acceptor. But with the depletion of nitrate the low potential of the system is likely to assert itself.

The oxalacetate - malate system occurs widely in biological systems and, like fumarate-malate, is a component of the Krebs cycle. Although this system, like its analogue, probably supplies active hydrogen, its contribution to the redox system in soil cannot be appreciable because of the poor poise of the system. The lack of poise is due to the extreme sensitivity of the enzyme which brings about the change to the slightest accumulation of the reaction product, oxalacetate (28).

Of the organic systems in soils, the most important are probably the two typical anaerobic systems, pyruvate-lactate and acetaldehyde-alcohol. Under aerobic conditions the reduced DPN* formed during glycolysis is reoxidized by atmospheric oxygen through the mediation of

* Diphosphopyridine nucleotide.

hydrogen carriers. When conditions become an aerobic, the reduced DPN is reoxidized at the expense of the reduction of pyruvic acid or products of pyruvic acid. This generates two redox systems, the pyruvate-lactate and the acetaldehyde-alcohol systems:



In view of the widespread occurrence of these systems and the relatively high concentrations in which they are found under anaerobic conditions, it is probable that they make an appreciable contribution to the redox systems in submerged soils.

The inorganic systems in the lower range of potentials are the $\text{Fe}^{+3} - \text{Fe}^{+2}$ and the sulphate-sulphide systems. The iron system has already been discussed and calls for only brief comment. From the position of the $\text{Fe}^{+3} - \text{Fe}^{+2}$ system on the redox scale, it would appear that appreciable concentrations of Fe^{+2} will be encountered only at relatively low potentials. Thus an appreciable reduction of manganese and virtual disappearance of nitrate will precede the appearance of Fe^{+2} . The findings of Mortimer (167) confirm these theoretical predictions.

The sulphate-sulphide system, unfortunately, is not amenable to similar theoretical treatment, owing to the anomaly presented by the $\text{SO}_4^{+4} - \text{SO}_3^{+3}$ system. The standard oxidation-reduction potential of this system at pH 7 calculated from the available information is lower than the potential of the hydrogen electrode at the same pH, while that of the $\text{SO}_3^{+3} - \text{S}^{+2}$ system is 0.3 volt higher on the scale. This means that the $\text{SO}_4^{+4} - \text{SO}_3^{+3}$ system does not exist, for any SO_3^{+3} formed is immediately reduced to S^{+2} . The behavior of the $\text{SO}_3^{+3} - \text{S}^{+2}$ system is more intelligible. The value of -0.19 volt for the standard potential at pH 7 is of the order of the potentials observed during sulphide formation in bacterial cultures (224) and in certain other sulfide systems (191).

Superimposed on the chemical and biochemical redox systems is the influence of the colloidal phase of soils. There is evidence that soil colloids can influence at least the E_h -pH relationship of soils. Kohnke (139) found that the E_h -pH curve for the $\text{Fe}^{+3} - \text{Fe}^{+2}$, which diverged markedly from that for soils, approached the latter when electro-dialysed clay was added to the system. Clay alone showed a linear relationship with a slope of .059. Puri and Sarup (190), working with Indian soils which had previously been leached with acid, obtained an average value of 53.4 mv per pH unit. They reaffirmed the opinion which Michaelis (156) had previously expressed that the colloidal phase functioned like a "metallic platinum-hydrogen-electrode."

(c) Factors that influence redox potentials of soils

The factors that influence redox potentials of soils are the

degree of aeration, the content of readily decomposable organic matter, and the base status of the soil. Good aeration, absence of excessive microbiological activity, and a low base status are conducive to high potentials. The opposite conditions favor low redox potentials.

The degree of aeration of a soil has a marked effect on the redox potential. Good aeration, with the consequent maintenance of a high oxygen concentration, gives high potentials, while any factor that tends to lower the oxygen concentration produces the opposite result. Numerous examples can be cited from the literature to illustrate this point but the majority of them are of a semi-quantitative character. Of these, the studies of Bradfield and co-workers (33) on the redox potentials of orchard soils of New York merit special mention because they constitute the first practical demonstration of the feasibility of using redox potential as an index of sub-soil drainage. On the basis of redox potentials of the soils in early spring they were able to segregate low yielding orchard sites associated with impeded drainage where measurements of ground water level alone were of little avail.

The few quantitative studies reported in the literature show the association of low oxygen concentrations with low redox potentials. They also indicate that oxygen concentration alone does not determine the value of the potential in the low range.

Mortimer (167) gives figures which show the variation of redox potential and oxygen concentration with depth in lake muds in contact with aerated water.

Depth in cm.	0	1-2	2-4	4-8
Dissolved O ₂ in mg/l	4.0	0.4	0.1	0.0
E _h at pH 7 in volts	0.50	0.20	-0.10	-0.10

The results of Pierce (187) show a much lower potential for comparable oxygen concentrations. His figures for the oxygen concentration and redox potential at a depth of 18" in the ground water of the transect of a moss peat bog are given below.

Dissolved O ₂ in p.p.m.	3.7	0.2	0.0	0.1	0.4	3.7
E _h at pH 7 in mv.	-107	-251	-262	-213	-207	-90

The analytical data of Pearsall for the oxygen concentrations and redox potentials at different depths in a lake are significant because they show that relatively low concentrations of oxygen are sufficient to maintain oxidizing potentials in lake water.

Depth in m.	6	7	8	9	10
Oxygen in mg/l.	6.4	6.0	0.8	0.4	0.3
E _h at pH 5	512	480	462	325	280

The influence of organic matter on soil potentials has been stressed by numerous investigators. Peech and Boynton (184) noted that waterlogging caused a marked drop in potential only in the case of soils containing readily oxidizable organic matter, and attempted to correlate susceptibility to reduction of certain New York soils on waterlogging to their C:N ratio. According to Pearsall (180) this ratio must exceed 20 for a marked drop of potential to occur on waterlogging. Burrows and Cordon (42) made the interesting observation that addition of casein and alanine to a drained soil gave highly positive potentials while glucose and starch had the opposite effect. These results throw additional light on the role of nitrate in stabilizing soil potentials at a relatively high value.

The close association between organic matter and redox potentials suggests that microbial activity is involved. Proof of this has been provided by the observation of Pearsall (178) and also of Peech and Boynton (184) that toluene arrests potential drifts and that low temperatures retard reduction.

2.3 Chemical Characteristics

The chemical properties of a soil undergo a drastic transformation on submergence. The oxidized constituents such as Fe^{+3} , Mn^{+4} , NO_3^- and SO_4^{++} that characterize a normal well drained soil virtually disappear and their place is taken by their reduced counterparts Fe^{+2} , Mn^{+2} , NH_4^+ and S^{--} . The course of organic matter decomposition is likewise diverted from carbon dioxide production to the generation of organic acids and methane. These changes are the chemical and biochemical consequences of oxygen deficiency.

2.31 The Reduction of Iron

The element iron occurs in soils in the form of primary minerals, silicate clays, and hydrated oxides and their organic and inorganic derivatives. Of these, the hydrated oxides are the most important because in soils they are the seat of the chemical and biochemical reactions involving iron. Present exclusively in the ferric state, these compounds impart to the soil the brown or reddish tints associated with good drainage. They are extremely insoluble in water and have a high capacity for fixing soluble phosphates added as fertilizer. On submergence, however, a marked change takes place. The brown or reddish-brown color changes to bluish-green or black shades, large amounts of iron are brought into solution, and the phosphate fixing power markedly reduced -- consequences of the reduction of ferric compounds to ferrous.

The chemical reduction of iron may be viewed from the angle of redox potential or oxygen concentration though essentially the reduction process is unitary.

A drop in redox potential, whatever its cause, should be accompanied by an increase in the concentration of the reduced phase, in this case Fe^{+2} . The theoretical increase which should accompany a given drop in potential may be calculated from the equation,

$$E_h = -0.10 + .058 \log \frac{1}{(\text{Fe}^{+2})}$$

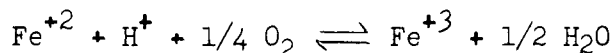
on the assumption that the concentration of Fe^{+2} is not affected by oxidation, precipitation, and complex ion formation. Substitution of 0.48 volt for E_h , for a well drained soil at pH 7 gives a Fe^{+2} concentration of 10^{-10} mols per liter. If as a result of submergence the potential drops to -0.10 volt the concentration of Fe^{+2} , according to this equation, becomes 1.0 mole per liter. This figure is never realized in practice because the simplifying assumptions made in the calculation are not strictly valid; but it indicates how great the increase in Fe^{+2} concentration accompanying a fall in redox potential can be.

The changes in concentration of Fe^{+2} may also be viewed from the standpoint of oxygen concentration. The expression,

$$p\text{Fe}^{+2} = 2 \text{ pH} + 1.93 - .25 p\text{O}_2,$$

which was derived earlier, may be used for this purpose. On substituting the value for the partial pressure of oxygen in air the concentration of Fe^{+2} at pH 7.0 turns out to be 10^{-16} mols per liter, a figure considerably lower than that obtained by a consideration of redox potential assuming there was no oxidation. The value 10^{-16} mols/liter is a better estimate of the Fe^{+2} concentration in a well drained soil than the one obtained ignoring the effect of oxygen and exemplifies the low concentration of iron in the solution of a well drained soil.

Quantitative treatment of the Fe^{+2} - O_2 relationship at very low oxygen tensions is rendered difficult by the absence of figures in the range 0 - .1 p.p.m. for oxygen concentrations in submerged-soil or comparable solutions. Another difficulty is that the reaction,



may not be truly reversible or its kinetics so slow at very low concentrations of oxygen that the expression,

$$p\text{Fe}^{+2} = 2 \text{ pH} + 1.93 - 1/4 p\text{O}_2$$

probably loses its validity.

The survey of the biochemical reduction of iron, fortunately, may be conducted on a firmer basis for there is abundant experimental evidence for the reduction of ferric iron as a result of microbiological activity. The role of bacteria in the transformations of iron is

described concisely by Halvarson (90): "The solution and precipitation of iron in nature are seen to be associated with equilibrium conditions which depend upon oxygen tension, carbon dioxide tension and acidity and the presence of organic compounds. These conditions may be modified extensively by bacterial activity. . . . Their effect upon the solution of iron can hardly be overemphasized in that they can effect changes favoring solution which do not occur spontaneously."

Starkey and Halvarson (223) were probably the first to demonstrate in a convincing manner the role of microorganisms in the reduction. They showed that a mixed soil inoculum, or a culture of Escheria coli or Clostridium sporogenes could reduce ferric hydroxide in a one percent glucose-mineral salts medium under both aerobic and anaerobic conditions. The reduction was more intense under anaerobic conditions. They observed ferrous iron concentrations as high as 740 p.p.m. even at a pH of 6.0 and concluded that the bulk of the iron was in the form of un-ionized organic complexes.

Ignatieff (108) concluded from the behavior of sterilized and unsterilized soil on waterlogging that the reduction of iron following flooding was largely a microbiological process.

Allison and Scarseth (11) provide striking proof of the efficiency of the reduction of iron as a result of bacterial activity. They found that, by incubating a soil with five percent sucrose anaerobically, free ferric oxide was removed as efficiently as by the rather drastic sodium sulfide-oxalic acid treatment.

The role of microbiological activity in the reduction of iron is further illustrated by the marked parallelism that Bloomfield (24) observed between the reduction of ferric oxide and the depletion of glucose when a London clay was incubated anaerobically in a glucose-mineral salts medium. The reduction and glucose depletion curves were roughly sigmoidal and showed the same lag periods. The reduction of iron ceased with the exhaustion of the glucose supply.

The findings of Yarkov and co-workers (254) are interesting because they bring out the effect of temperature and of the presence of sodium nitrate on the reduction of iron. Incubation of a waterlogged soil at 0°C for 12 days caused hardly any increase in ferrous iron while at 30°C there was a marked increase. The presence of sodium nitrate retarded the reduction, the effect increasing with nitrate concentration. In the presence of sugars, sodium nitrate did not prevent the reduction of iron.

These experiments illustrate the efficiency of anaerobic bacteria in reducing ferric iron but throw no light on the mechanism of the process. In this connection the finding of Roberts (202) that, of 265 cultures tested for their ability to reduce iron on soil colloids with glucose as the source of energy, only certain strains of B. polymyxa were efficient reducers of Fe^{+3} would, at first sight, suggest that the

reduction is species specific and therefore in all probability an intrinsically biological reaction. But Bromfield (39) while adding another organism -- B. circulans -- to the short list of Fe^{+3} reducers pointed out that unsuitability of the culture media may account for the failure of more organisms to function as iron reducers. Further, comparing the behavior of B. polymyxa (an efficient reducer of Fe_2O_3) with that of nitrate and sulfate reducing bacteria he came to the significant conclusion that the reduction of ferric hydroxide by B. polymyxa was not intrinsically a microbiological reaction. Bloomfield (25, 26) by an entirely different approach came to a conclusion of wider application, namely that ferric oxide can be reduced by the products of the microbial decomposition of organic matter without the direct intervention of microorganisms.

Bloomfield (25) observed that an extract of dried grass caused reduction of ferric oxide in sterilized soil and inferred that either reducing bacteria were present in the grass or the process was not intrinsically microbiological. He then showed how a grass fermented in the absence of ferric oxide gave extracts which were capable of causing rapid reduction of ferric chloride -- "a reduction too rapid to be caused by microbial action." In a further experiment he showed that a sterile extract of fermented grass could reduce ferric oxide on sterilized soil. But the amount of ferric iron reduced was much less with the soil than with ferric chloride. Bloomfield therefore concluded that the rate of solution of ferric oxide was a limiting factor. More recently Bloomfield (26) has suggested that non-biological solution and reduction of iron can take place even under neutral and aerobic conditions, by aqueous extracts of pine needles or Kauri leaves. Schnitzer and Delong (210) have confirmed this observation under field conditions: they showed that even the canopy drip from a forest had the ability to dissolve and reduce ferric iron.

The evidence is clear that submergence of a soil brings about conditions eminently suitable for the reduction and solution of iron, especially if decomposable organic matter is present. The next problem is the elucidation of the nature of the reduced products.

Although large amounts of ferric iron may be reduced when a soil is submerged the concentration of ferrous ions in the soil solution is relatively small owing to the precipitation of ferrous hydroxide, carbonate, and sulfide. The precipitation reactions are governed by ionic equilibria involving Fe^{+2} and OH^- ions, carbon dioxide, and hydrogen sulfide.

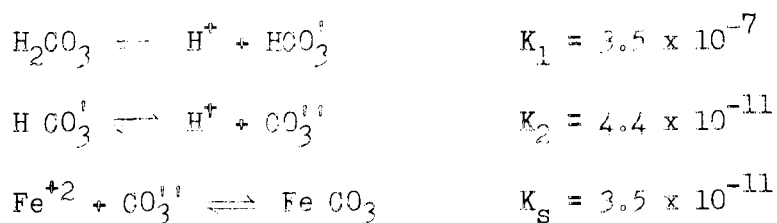
Theoretical treatment of the precipitation of ferrous hydroxide is difficult because of the uncertainty about the value of its solubility product. According to Arden (16) ferrous hydroxide separates out as a white precipitate at a pH of 8.1 from 0.05 molar ferrous sulfate if oxygen and Fe^{+3} are completely excluded. Under these conditions the solubility product of ferrous hydroxide is approximately 2.4×10^{-14} . If the smallest amount of Fe^{+3} is present, ferrous hydroxide is precipitated as a green gelatinous mass at a pH of 6.4, giving an apparent solubility

product of 6.4×10^{-18} . If air is not completely excluded, precipitation occurs at a pH of 5.25 compared with the pH value of 5.49 at which Britton (36) observed the same phenomenon. The solubility product of ferrous hydroxide is now reduced to a still lower value, viz., 5.3×10^{-20} . Since a highly reduced soil is practically devoid of oxygen the intermediate value of 6.4×10^{-18} may be taken as the solubility product of ferrous hydroxide. On this basis a highly reduced submerged soil at pH 7 may have about one millimol per liter of ionic ferrous iron in solution. The relationship between the concentration of Fe^{+2} in solution and pH may be shown as follows:

$$p \text{ Fe}^{+2} = 2 \text{ pH} - 10.8$$

In a submerged soil, especially under the conditions favorable to intense reduction, the carbon dioxide concentration is several hundred times its value in air. Carbon dioxide is therefore likely to exert a considerable influence on the precipitation and solution of ferrous iron. The solubility product of ferrous carbonate is 3.5×10^{-11} . If the carbon dioxide tension is taken as 0.1 atmosphere, a reasonable figure for a submerged soil, at pH 7.0, the CO_3^{+1} concentration is approximately 6×10^{-5} mols per liter. This concentration of CO_3^{+1} is sufficient to precipitate Fe^{+2} at a concentration as low as 6×10^{-7} mols per liter. Practical verification of this deduction comes from the frequent occurrence of the mineral siderite (177), and ferrous carbonate of more recent origin in bogs (90). Further, Halvarson (90) claims to have obtained a white precipitate of ferrous carbonate during the anaerobic fermentation of peptone medium by a soil inoculant in the presence of iron filings.

By analogy with the behavior of the carbonates of other bivalent metals it may be supposed that with increase of carbon dioxide concentration, some of the FeCO_3 may be brought into solution as bicarbonate. Theoretical treatment of so complex a system as a submerged soil is difficult but certain broad conclusions may be drawn from a study of the simple $\text{Fe}^{+2} - \text{H}_2\text{CO}_3$ system. For this system the following equilibria hold:



If any $\text{Fe}(\text{HCO}_3)_2$ formed is assumed to be completely ionized the following expression can be derived:

$$\left[\text{Fe}(\text{HCO}_3)_2 \right]^2 = \frac{K_1 K_s}{4K_2} \cdot \left[\text{H}_2\text{CO}_3 \right]$$

where the square brackets denote concentrations. This can be expressed as:

$$p\text{Fe}(\text{HCO}_3)_2 = 2.38 + 1/3 p\text{H}_2\text{CO}_3$$

where the symbol p has the usual significance. At a CO_2 pressure of 0.1 atmosphere and in the complete absence of oxygen, the concentration of ferrous bicarbonate, according to this equation, may be of the order of one millimol per liter. If oxygen is present it is precipitated as ferric hydroxide. According to Einsele an oxygen concentration of 0.5 mgm per liter is sufficient for this.

The equilibria which govern the interaction of Fe^{+2} and H_2S are:



The solubility product of ferrous sulfide is so small that a Fe^{+2} concentration of 10^{-3} mols per liter will keep the sulfide ion concentration down to 3.7×10^{-16} mols per liter. The relationship between Fe^{+2} and H_2S which is of greater practical significance, is given by the expression,

$$\frac{K_1 K_2}{K_s} = \frac{(\text{H}^+)^2}{(\text{Fe}^{+2})(\text{H}_2\text{S})}$$

or
$$p\text{Fe}^{+2} = -3.52 + 2p\text{H} - p\text{H}_2\text{S}$$

It will be seen from this equation that at pH 7.0 and an Fe^{+2} concentration of 10^{-3} mols per liter the concentration of H_2S is of the order of 10^{-8} mols per liter. Thus the presence of iron should keep the concentration of H_2S down to a very low value. Experimental evidence is in perfect harmony with theory. Mortimer (166) and Misra (160) could detect no free H_2S in strongly reduced lake muds, although FeS was present. Starkey and Wight (224) report similar findings. And most interesting of all Mitsui (161) and Shioiri and Tanada (213) report that injury to rice from H_2S occurs only in the degraded rice soils very low in iron and manganese. One of the methods of minimizing the injury is the addition of red upland soil to the degraded fields (213).

From this discussion it would appear that ferrous iron in the form of the Fe^{+2} ion can exist in solution in a highly reduced medium up to concentrations of the order of one millimol per liter at a pH of 7.0. But there is abundant evidence that the concentrations of ferrous

iron in highly reduced media often exceed ten times this figure. Starkey and Halvarson (223) found ferrous iron in concentrations as high as 740 p.p.m. in solution near neutrality. Bloomfield (25, 26) furnished very clear evidence not only for the presence of ferrous iron in high concentrations but also for the stability of these solutions even towards alkali and to a lesser degree towards air. Clearly, a high proportion of the ferrous iron is not in the ionic form. This was recognized by these workers who suggested that the ferrous iron was present in the form of organic complexes which are only slightly dissociated. Mortimer (166) came to a similar conclusion regarding ferrous iron in reduced lake waters. This behavior of iron is readily understood when it is recalled that the iron both in the ferrous and ferric states has a strong tendency to fill up its unoccupied orbitals by complex formation and attain the stable electronic configuration of the next inert gas in the periodic table, krypton. The complex may be formed by the ion accepting individual donor molecules or by linking up with two or more donor groups of a single molecule. In the latter case a chelate is formed. These are important because they have exceptional stability. Now the decomposition of organic matter under anaerobic conditions supplies chelating agents par excellence for complex formation. Among them are: α -hydroxy carboxylic acids, dicarboxylic acids, hydroxy dicarboxylic acids, hydroxy and dicarboxylic amino acids and the sulfur containing amino acid cysteine. Thus a submerged soil may hold in solution quantities of ferrous iron far in excess of the amounts permitted by the ionic equilibria involving H^+ ion concentration, partial pressure of CO_2 and H_2S and even O_2 tension. Also, the possibility cannot be excluded of the formation of insoluble organic complexes of ferrous iron, for insoluble organic complexes of iron have been shown by Bremner and co-workers (34) to be present in soils.

Although an undetermined proportion of the ferrous iron in the solution of a submerged soil is undoubtedly in the form of practically undissociated complexes, theory indicates that ferrous ion in the ionic state may be present in a submerged soil solution to the extent of approximately one millimole per liter at pH 7. This raises the important question: to what extent do ferrous ions displace exchangeable cations from the soil colloids? The available evidence suggests that this reaction takes place to an appreciable extent. Mortimer (166) noted an increase in electrical conductivity of water in contact with the reduced mud of lakes. He apportioned the increase to increases in concentration of ferrous iron and ammonia. The residual increase he attributed to the liberation of bases from the reduced mud. Ignatieff (108) found that potassium chloride extracts of reduced soils contained ferrous iron far in excess of aqueous extracts and concluded that Fe^{+2} functioned as an exchangeable cation. Bloomfield (24) observed that when London clay was incubated anaerobically with glucose in a medium whose final pH was 4.5-5.0 less than ten percent of the total iron reduced was associated with the clay. The high proportion of iron in solution was no doubt due to the rather high acidity of the medium.

The displacement of exchangeable cations from the colloidal complex has two important consequences. First, the supply of readily available potassium, calcium and magnesium is increased and secondly

these constituents may be lost by drainage. This loss of bases, according to Robinson (230), is one of the causes of infertility of poorly drained soils.

2.32 Reduction of Manganese

The transformations of manganese initiated by submergence are similar to those of iron; the few differences that exist are ones of degree rather than of kind.

In a well drained soil the reactive forms of manganese are the higher oxides (MnO_2 , Mn_2O_3 , Mn_3O_4), divalent manganese (exchangeable Mn^{+2} and Mn^{+2} in solution) and complexes of divalent and trivalent manganese. The higher oxides resemble ferric oxide in their low solubility in water but differ from it in that they are more readily reduced. Conversely, divalent manganese being more stable towards oxygen and more soluble than divalent iron is found in higher concentration than iron in well drained soils. The quantitative relationship between the Mn^{+2} concentration on the one hand, and H^+ ion concentration and oxygen tension on the other, is given by the expression,

$$\text{pMn}^{+2} = 0.0 + 2\text{pH} - 1/2 \text{pO}_2$$

obtained by combining the equations for the potentials of the $\text{MnO}_2 - \text{Mn}^{+2}$ and $\text{O}_2 - \text{H}_2\text{O}$ systems. In this expression pMn^{+2} and pO_2 stand for the negative logarithms of the concentration of Mn^{+2} in mols per liter and partial pressure of oxygen in atmospheres, respectively. It is clear from this equation that the concentration of Mn^{+2} in a well drained soil at pH 7 though low, is more than one hundred times the concentration of Fe^{+2} (10^{-16} mols per liter) under the same conditions.

There is evidence that these reactive forms of manganese are in a state of dynamic equilibrium and several investigators (69, 80, 150) have postulated the existence of a manganese cycle in soils to describe it. The two chief components of the cycle are (a) the reduction of the higher oxides of manganese as a result of increased H^+ ion concentration, lowered oxygen tension, and biological activity. (b) The oxidation of Mn^{+2} to the higher valence states caused by decrease in H^+ ion concentration, increase in oxygen tension, and by the activities of certain bacteria that oxidize Mn^{+2} to MnO_2 . In a submerged soil the oxidative part of the cycle is completely suppressed owing to the virtual absence of oxygen while the reduction process proceeds unimpeded if biological activity is favored by the presence of readily decomposable organic matter.

There is abundant evidence that the reduction of manganese is largely a consequence of microbiological activity. A few examples are selected to illustrate the salient features of the process.

Among the earlier studies on the reduction of manganese is Piper's (188) classic investigation of the factors governing the availability of manganese in soils. He noted among other things that the addition of glucose to a waterlogged soil caused a marked increase in the amount of water soluble manganese. The addition of glucose was accompanied by a great increase in bacterial activity. Water-logging alone brought into solution manganese even at a pH of 8.0.

Fujimoto and Sherman (80) found that the addition of organic substances to a soil caused a marked increase in the level of exchangeable Mn^{+2} . Their figures show that with increasing applications of sugar, pineapple leaves, or sugarcane leaves, the level of exchangeable Mn^{+2} increased. With pineapple and sugarcane leaves release of Mn^{+2} was apparent at the end of twenty-four hours. On further standing the level of exchangeable manganese rose to extremely high levels with the higher applications of organic substances.

The studies of Hurwitz (106) on the effect of temperature on the reduction of soil manganese in the presence of oat straw and alfalfa meal show that the kinetics of manganese reduction are those of a reaction brought about by proliferating microorganisms. He found that the content of exchangeable manganese showed no appreciable rise below $30^{\circ}C$. The rate of formation of Mn^{+2} increased rapidly in the range of 37° - $47^{\circ}C$. The peak rate of manganese reduction (which was observed on the third day of incubation) was a logarithmic function of the temperature above $30^{\circ}C$.

Mann and Quastel (150) showed the analogy between the kinetics of manganese reduction and the depletion of the glucose supply when a soil was perfused with glucose solution.

The experiments of Christiansen and co-workers (49) illustrate the effect of pH and moisture content on the reduction process. The results show that low pH and low moisture content, both of which retard bacterial activity, caused a prolonged release of Mn^{+2} though in smaller amounts, than pH and moisture conditions better suited to bacterial activity. At a pH near neutral and moisture conditions near optimum the release of Mn^{+2} was much greater but short lived.

The evidence is clear that microbial activity causes manganese reduction but it is not certain whether the reduction is due to a direct coupling of the process to metabolic processes or whether it is due to the decomposition products of organic matter. The findings of Mann and Quastel (150) seem to suggest that it is due to both.

Mann and Quastel found that MnO_2 is easily reduced to Mn^{+2} by sulfhydryl compounds such as thioglycollic acid and cysteine or by polyhydric phenols such as hydroquinone, catechol and gallic acid. They noted further that bacterial suspensions in the presence of suitable hydrogen donors and traces of hydrogen carriers such as pyocyanine or methylene blue could bring about reduction of MnO_2 and concluded: "These facts show that the reduction of MnO_2 can be accomplished either by bacterial masses in the presence of their hydrogen donors and carriers or by

thiols or polyphenols, elaborated in the process of bacterial or plant metabolism or in the breakdown of soil organic matter. It follows that the reduction of MnO_2 in soils is a process which may be accomplished entirely by biological means. Many species of bacteria may be involved in the reduction, the determining factors being the supply and the nature of organic matter present."

If the transformation of manganic oxides to manganous takes place so readily in aerobic soils, then, under submerged conditions the reduction should proceed with incomparable ease. The absence of oxygen, the metabolism of anaerobic bacteria, and the generation of powerful reducing agents by the anaerobic decomposition of organic matter should all combine to make the reduction of manganese in a submerged soil a very efficient process indeed. Apparently the only factor that prevents a submerged soil from being deluged with reduced manganese is the low content of the element in most soils. According to the figures of Marbut (151) for some representative American soils the content of manganese (as MnO) varies from 0.007 to 0.44 percent compared with 1.75 to 6.12 percent for Fe_2O_3 .

Subsequent to reduction, the transformation of manganese in a submerged soil may be assumed to follow the pattern of ferrous iron. Thus manganese may be present in a submerged soil as the hydroxide, carbonate, bicarbonate and sulfide. But on account of the greater solubility of these compounds than the corresponding ferrous ones it is unlikely that a high proportion of the reduced manganese will be present in the solid phase except as an exchangeable ion. The ease with which manganese forms organo-metallic complexes implies that, as with iron, appreciable amounts of reduced manganese may be present in the form of complexes. Heintze and Mann (101) have furnished evidence for the presence of divalent manganese in mineral and organic soils.

2.33 Increase in Solubility of Phosphate

When a soil is submerged the availability of phosphate, whether judged by plant response or chemical tests, increases.

The first suggestion that submerging a soil causes an increase in the solubility of phosphate is found in the observation of Bartholomew (21) that in Arkansas rice showed no response to phosphatic fertilizers even on soils low in phosphate, though his explanation must, in the light of recent research, be considered erroneous. Beacher (22), in a recent report on rice fertilization in Arkansas apparently confirms this observation when he refers to "the generally inconsistent results from superphosphate on rice soils known to be low in available phosphorus" but, like Bartholomew, offers no satisfactory explanation. The identical phenomenon was observed extensively by Japanese workers who were, however, quick to recognize its theoretical significance. Aoki (14) reported that rice grown under lowland conditions gave no response to phosphatic fertilizers while barley grown on the same soil as a winter crop did and attributed

this to the reduction of insoluble ferric phosphate to the more soluble ferrous phosphate. Mitsui (161) has recently furnished further details of the behavior of rice towards phosphatic fertilizers. He reports that rice grown on fields fertilized with superphosphate rarely responds to additional applications of phosphatic fertilizers for some years although winter crops grown on the same fields under upland conditions do respond. He states further that the residual effect of phosphate applied to the upland crop is remarkable when the succeeding crop is rice but the effect of phosphate, applied to rice, on the upland crop following it is negligible.

These observations strongly suggest that phosphate is rendered more available under flooded conditions but the possibility cannot be excluded that the lower supply of available phosphate to the dryland crop grown in winter in rotation with rice may be due to the retarding effect of low temperature on the mineralization of organic phosphates and other processes influencing phosphate availability, and also to the smaller amount of phosphate in solution. Clear cut evidence for the reality of the increase in availability of phosphate in a reduced soil comes from chemical tests.

Mortimer (166) noted that when the surface layer of lake muds underwent reduction as a result of the depletion of oxygen in the hypolimnion following thermal stratification the concentration of phosphate in the water increased over a hundredfold. Yarkov and co-workers (254) found that phosphate extractable with 0.5 N acetic acid increased when a water-logged soil was incubated at 30°C. There was a simultaneous increase in ferrous iron and a drop in redox potential. McGregor (153) reports that 0.5 N acetic acid soluble phosphate was highest in poorly drained neutral spots and lowest in well drained acid areas; when superphosphate was added to the soil the increase in acetic acid soluble phosphate was greater and of longer duration on poorly drained soil than on well drained soil; further, there was appreciable downward movement of phosphate in poorly drained soil while in well drained soil the applied superphosphate was confined to the top three inches.

Finally, there are Fujiwara's (81) findings that the response of lowland rice to iron and aluminum phosphates was markedly superior to that of barley and that ferric phosphates were superior to aluminum phosphates as source of phosphate for lowland rice.

It is clear from these examples that when a soil undergoes reduction there is an increase in both water soluble and acetic acid soluble phosphate. The increase in water soluble phosphate may be due to (a) the reduction of ferric phosphate to ferrous phosphate; (b) hydrolysis of ferric and aluminum phosphates due to increase in alkalinity; (c) displacement of phosphate from ferric and aluminum phosphates by complexing agents produced by the anaerobic decomposition of organic matter; (d) anionic exchange between phosphate adsorbed on the clay and organic anions; and (e) hydration of ferric and aluminum phosphates. The increase in solubility in acetic acid may be attributed to all of

*from
p. 254*

the above reactions plus the greater accessibility of calcium phosphates brought about by the removal of protective coatings of ferric oxide. Of these factors, the reduction of ferric phosphate is probably the most important.

There is abundant evidence that iron compounds in soils especially the hydrated ferric oxides have a marked capacity for fixing phosphate though the exact mechanism is by no means clear. Submergence of a soil would cause an increase in soluble phosphate (a) if these compounds are reduced, (b) if ferrous phosphate is more soluble than ferric. There is evidence for both. Bromfield (39) has shown that FePO_4 is reduced by Bacillus circulans as readily as $\text{Fe}(\text{OH})_3$. Eriksson (75) has determined the solubility $\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ and given an expression for the solubility product which may be written as

$$\text{pH}_2\text{PO}_4' = -6.0 - 1.5 \text{pFe}^{+2} + 2\text{pH}$$

It is clear from this equation that at a Fe^{+2} concentration of one millimol per liter and pH 7.0 the concentration of $\text{H}_2\text{PO}_4'$ is $10^{-3.5}$. In other words, the solubility of ferrous phosphate is so high that under the conditions obtained in a submerged soil any ferrous phosphate formed would be completely in solution. The rare occurrence of the mineral vivianite is therefore not surprising.

The solubility of ferric and aluminum phosphates is lowest in the pH range 3.0 - 6.0 (247). The increase in solubility above pH 6.0 is presumably due to hydrolysis. Aoki (14) has studied the behavior of phosphate under flooded and upland conditions. His findings are that under both upland and lowland conditions solubility of phosphate was minimum in the pH range 5-7. Under lowland conditions the solubility below pH 5 and above pH 7 was markedly higher than under upland conditions.

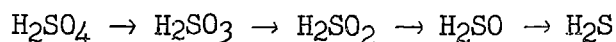
The ability of complexing agents like oxalate and citrate and certain unidentified components of soil organic matter to displace phosphate from clays and the hydrated oxides of iron and aluminum has been so clearly demonstrated for well drained soils that the possibility of this operating in a submerged soil hardly needs emphasis.

2.34 Reduction of Sulfate

Sulfides are invariably present in soils which have been under water for any appreciable length of time. They are derived chiefly from the reduction of sulfates.

The reduction of sulfate to sulfide is brought about by a small group of bacteria. Sulfate is the specific hydrogen acceptor in the oxidations which provide the energy for the metabolic processes of these bacteria. Being strict anaerobes they function best only at extremely

low redox potentials (224). They are active in the pH range 5.5 - 8.5 and derive their energy from readily decomposable organic matter and molecular hydrogen (224). According to Baars (18) the reduction proceeds in the following stages:



The intermediate products are extremely transitory. The hydrogen sulfide formed is almost completely removed by precipitation chiefly as ferrous sulfide in normal submerged soils but in soils very low in iron such as the degraded rice soils of Japan hydrogen sulfide can accumulate in amounts toxic to rice (161, 213).

Starkey and Wight (224) have shown that the sulfate reducing bacteria can bring about a marked decrease in redox potential. This effect is less pronounced at low sulfate concentrations apparently because the activities of these bacteria are retarded. If the very low potentials often encountered in submerged soils are due to sulfate-reducing bacteria the findings of Starkey and Wight suggest that they may be avoided by excluding the use of fertilizers carrying sulfate.

In view of the sensitivity of sulfate reducing bacteria to acidity it is interesting to note that the injurious effects of ammonium sulfate on certain soils, on which H_2S toxicity is a problem, is minimized by controlling the pH between 5 - 5.5 (131) and aggravated by liming (176).

2.35 Transformations of Nitrogen

The nitrogen regime in a submerged soil is characterized by the virtual absence of nitrate and by the accumulation of ammonia.

The disappearance of nitrate under anaerobic conditions is so well established that citing the evidence for it is a work of supererogation. This review will therefore be restricted to the mechanism of the process and the factors that influence it.

The loss of nitrate from a submerged soil may be due to assimilation by plants, leaching, denitrification, and reduction. It has also been suggested that substantial amounts may be immobilized by microorganisms (63). Denitrification refers to the loss of nitrate as nitrogen or its oxides and reduction, to the conversion of nitrate to ammonia. Both these processes are probably biochemical in nature.

The role of microorganisms in denitrification was recognized over seventy-five years ago and several specific denitrifying organisms are reported to have been isolated subsequently (244). There is sufficient evidence now to indicate that denitrification is not restricted to a narrow group of microorganisms but is a phenomenon of much wider

occurrence resulting from the biochemical reaction between nitrate and the products of anaerobic metabolism. Denitrification, then, should be favored by low oxygen tension and by the presence of readily decomposable organic matter.

The importance of both these factors has been recognized for nearly a hundred years but quantitative studies have been few in number and recent in origin. Of these, the investigations of Broadbent are of special interest.

Broadbent (37) studied the effect of oxygen tension and level of organic matter on the loss of nitrate from soils under laboratory conditions. His figures clearly show that low oxygen tension and the presence of organic matter favor denitrification although the aspect emphasized by the author is the hitherto unsuspected phenomenon of active denitrification even in aerobic soils. His finding that utilization of oxygen in the nitrate for oxidation of organic matter was noticeable only at the low oxygen concentration of 0.14 percent is of special interest in view of the role assigned to nitrate as a hydrogen acceptor, in the treatment of redox systems in soils. More to the point presently under discussion are his observations that below 4.5 percent oxygen all nitrate disappeared even from soils which received no additional organic matter and that in the presence of ground clover losses of nitrogen occurred at all oxygen levels.

The effect of oxygen tension and the presence of organic matter on denitrification is brought out even more clearly in a recent paper by Broadbent and Stojanovic (38). They noted that at an oxygen tension of 0.1 percent the loss of nitrate from a soil incubated for ten days was 80 percent compared with a loss of 16 percent when the oxygen tension was 19 percent. In a further experiment they observed that the loss of nitrogen was greatest when a low oxygen tension (0.1 percent) was combined with a high level of organic matter (2 percent corn leaves).

The experimental evidence clearly indicates that low oxygen tensions and the presence of organic matter favor denitrification. Thermodynamical considerations, as pointed out by Broadbent (37), lead to the same conclusion. But there is considerable disagreement about the relative importance of the two factors. Broadbent (37) was led by theoretical and experimental evidence to the view that although a low oxygen tension favors denitrification it is not a necessary condition. He concluded: "Denitrification rate is affected more by the quantities of nitrate and oxidizable carbon in the soil than by partial pressure of oxygen." Lloyd (148), a decade before had reached a somewhat similar conclusion: he felt that the limiting factor in denitrification by marine bacteria was the supply of organic matter. In sharp contrast with these views, Wiljer and Delwiche (248) recently reported that initial nitrate concentration did not influence the rate of denitrification and that an oxygen tension as low as 5 mm. of mercury reduced the rate of denitrification to one-tenth of the anaerobic denitrification rate, even in the presence of added organic matter. The little denitrification

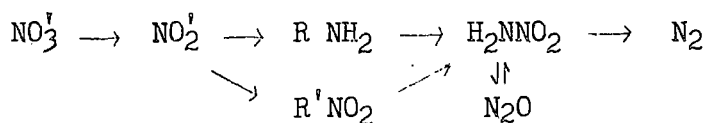
observed under atmospheric conditions, they suggested, might have been due to small anaerobic pockets. These conflicting findings leave the relative importance of low oxygen tension in denitrification unsettled. The relative effect of organic matter is no clearer. Broadbent (37) reported that denitrification took place from soils containing no fresh organic matter even under aerobic conditions. Even more surprising is Jones' (119) report that the addition of 0.5 percent sucrose to an anaerobic soil did not increase the rate of denitrification over the soil with no sucrose.

A third factor which affects the rate of denitrification is the pH of the soil. Denitrification is believed to be favored by a neutral to alkaline reaction (244, 248). The experimental evidence clearly points to this but there is no agreement about the optimum pH range. Lloyd found that pH 8.0 - 8.4 was the most favorable range for denitrification by marine bacteria. Broadbent (37) reported that denitrification losses were greatest at pH 6.3. Wiljer and Delwiche (248) observed that denitrification rates were independent of pH above a value of 6.3; below pH 6 denitrification rates were slightly retarded but even at pH 4.9 more than 70 percent of the nitrate was lost in two weeks. Jansson and Clark (113) obtained clear evidence of the reduction of nitrogen losses during the anaerobic decomposition of plant materials in the presence of nitrate by low pH and attributed it to the toxic effect of nitrous acid on the bacteria that brought about the change. In general agreement with these findings is the observation of De and Sarkar (63) that a soil whose pH was 8.3 had its nitrate content reduced from 52 p.p.m. to 0.3 p.p.m. after fifteen days of submergence while a lateritic soil (pH 5.1) with approximately the same initial nitrate content had a nitrate content of 19.4 p.p.m. even thirty days after submergence.

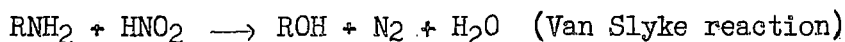
The products of denitrification are nitric oxide, nitrous oxide and nitrogen. Of these, until very recently, nitrogen was believed to be the most important. In the past few years, however, increasing importance has been attached to the oxides of nitrogen. Broadbent and Stojanovic (38) drew attention to the numerous reports about the presence of nitrous oxide in the atmosphere and indicated that it could be a denitrification product from even aerobic soils. Arnold (17) concluded from laboratory and field studies: "Nitrous oxide evolution is a factor of considerable significance to the nitrogen economy of soils. Soils which are approaching saturation with moisture rapidly release large amounts of their available nitrogen as nitrous oxide. At low moisture contents very slow evolution of nitrous oxide can take place." Wiljer and Delwiche (248) followed denitrification quantitatively using N^{15} as tracer. They found that nitrous oxide was the main product of denitrification under most soil conditions. pH had a marked effect on the composition of the gas formed by denitrification. Above pH 7 nitrous oxide was the major product but it was reduced to nitrogen if allowed to remain in the system. They concluded from this that in a submerged soil which is neutral or alkaline the nitrous oxide formed at lower depths would be reduced to nitrogen during its upward diffusion in solution. At low pH values they noted that the proportion of nitric oxide increased

and at pH 4.9 nitric oxide and nitrous oxide were produced in equal volumes.

The exact mechanism of denitrification is not known. Allen and van Niel (8) using the technique of simultaneous enzyme adaption found that nitrate, nitrite and nitrous oxide (the last when conditioned) behaved as intermediates. Nitramide, too, had the properties of an intermediate. On this basis they gave the following hypothetical scheme for denitrification:



In this scheme all the nitrogen in the products of denitrification is assumed to have come from nitrate because Allen and van Niel found no evidence of any nitrogen from amino, amide or bacterial nitrogen. But the possibility cannot be excluded of the following chemical reaction, especially at low pH values:



And, indeed, Pearsall (180) has suggested that ammonium nitrate as a fertilizer for lowland rice had the "theoretical disadvantage" of being likely to be lost even more readily than other nitrates, presumably by the Van Slyke reaction. The evidence is completely against this view. Jones (119) using $\text{N}^{15}\text{H}_4\text{NO}_3$ showed that in the pH range 4.0 - 6.0 only the faintest trace of nitrogen came from the Van Slyke reaction. Allison and co-workers (10) observed that at the nitrate concentrations found in soils no nitrogen was given off by this reaction above pH 4.1 and concluded that loss of gaseous nitrogen by the Van Slyke reaction was improbable.

Wiljer and Delwiche (248) were more categorical. They concluded from their studies on denitrification, by the isotopic technique, that "both nitrogen atoms in N_2O and N_2 , as well as the nitrogen atom in the NO were exclusively derived from nitrate."

Loss of nitrate by reduction to ammonia appears to be insignificant. De and Sarkar (63) were led to this conclusion by the marked disparity between the amount of nitrate lost and the amount of ammonia formed in a water-logged soil. Broadbent and Stojanovic (38) using more refined techniques found that the loss of nitrate by reduction to ammonia amounted to only 0 - 6 percent in a whole series of experiments. More recently Wiljer and Delwiche (248) reported that reduction of nitrate to ammonia was very small; it increased slightly when the amount of organic matter was raised to an inordinate level.

Nitrite, an intermediate product of denitrification and nitrate reduction, is invariably present in submerged soils. But its importance

has been grossly over-rated. The mistaken notion that nitrates can accumulate in high concentrations in submerged soils stems from the findings of early workers. But the highly artificial conditions under which some of these results were obtained is not generally realized. Daikuhara and Imaseki (56) are frequently cited as having shown that nitrates accumulate in high concentrations when nitrates are applied to rice soils. But these are the details of one of their experiments: 3.5 gm. sodium nitrate were added with 5.0 gm. starch to 700 gm. soil and 150 c.c. of a solution of K_2HPO_4 and $MgSO_4$; after ten days the nitrite content was found to be 0.35 percent as KNO_2 . In contrast to this exceedingly high concentration of nitrite obtained under intensive conditions, the levels of nitrite reported for submerged soils, including those fertilized with nitrate, under greenhouse or field conditions lie in the range 0-3 p.p.m. (63, 112, 127, 198, 227).

The accumulation of ammonia, like the disappearance of nitrate, is a striking feature of nitrogen transformations in submerged soils. Clearly intelligible on the basis of the well known principles of the transformation of nitrogen in aerobic soils, the phenomenon is substantiated by innumerable experiments under laboratory, greenhouse and field conditions.

The mineralization of organic nitrogen (proteins) in an aerobic soil may be represented as follows:

proteins $\longrightarrow$ polypeptides $\longrightarrow$ amino acids $\longrightarrow$ ammonia $\longrightarrow$ nitrate $\longrightarrow$ nitrite.

The degradation to the ammonia stage is the work of general purpose heterotrophic organisms including fungi, bacteria and actinomycetes while the subsequent nitrification is effected by highly specific, aerobic, autotrophic bacteria. On submergence, nitrification is suppressed but the process of ammonification continues though with considerable modifications. Thus ammonia accumulates in a submerged soil.

Janssen and Metzger (112) furnish a striking illustration of the alteration in the course of nitrogen mineralization caused by submergence. They studied the changes in nitrate and ammonia in a soil heavily manured with vetch, under well drained and submerged conditions. In the well drained soil ammonia rose to 12 p.p.m. in the soil solution at the end of two weeks and declined to practically nothing at the end of six weeks while nitrate steadily increased and attained a level of 40 p.p.m. in the soil solution at the end of 10 weeks. In the case of the submerged soil ammonia increased steadily from the time of submergence until it reached a level of 30 p.p.m. in the soil solution. The total amount of ammonia liberated no doubt was considerably higher than the concentration in the solution would indicate. From similar experiments under laboratory and field conditions Joachim and Kandiah (117) concluded that green manuring of paddy fields in the puddled state was preferable to early green manuring in the semi-dry state. When green

manure was applied to puddled fields nitrogen was released in the form of ammonia and was assimilated by the crop. Green manuring when the soil was in a semi-dry state resulted in nitrification and loss of nitrogen by leaching and denitrification on subsequent flooding.

Although ammonia production continues under submerged conditions it can be predicted from theory that this is a considerably modified version of ammonification under aerobic conditions.

Ammonification in an aerobic soil is effected by a wide group of microorganisms of which the fungi are normally the most vigorous. On submergence the fungi are replaced by the somewhat sluggish anaerobic bacteria so ammonification and immobilization of nitrogen should both be retarded.

The aerobic metabolism of fungi with its high energy release enables this group of organisms to carry on a vigorous decomposition of organic matter coupled to synthetic activity at a high level. Thus decomposition is rapid but the release of nitrogen is nil unless the substrate has a C:N ratio less than 16 (244). Anaerobic bacteria, on the other hand, operating at the low fermentation energy levels synthesize much less cell material. Thus the nitrogen factor and nitrogen equivalent for the decomposition of organic matter should be less under anaerobic conditions than under aerobic conditions. The results of Acharya's experiments provide a striking illustration of these deductions.

Acharya (3) studied the decomposition of rice straw under aerobic, partially aerobic and strictly anaerobic conditions. He found that the rate of decomposition of the straw, the nitrogen factor,* and the nitrogen equivalent** were highest under aerobic conditions and lowest in the strictly anaerobic treatments. His figures show the marked decrease in both nitrogen factor and nitrogen equivalent for the decomposition of straw when conditions change from aerobic to anaerobic.

	Nitrogen factor	Nitrogen equiv.
Aerobic	0.54	1.1
Partially aerobic	0.40	0.96
Strictly anaerobic	0.07	0.17

The number of grams of additional nitrogen required to decompose 100 grams of straw was reduced from 0.54 to 0.07 while the amount of nitrogen immobilized was reduced from 1.1 to 0.17 gm. per 100 gm. straw decomposed by the change from aerobic to anaerobic conditions.

Sircar and co-workers (217) reported similar results. They noted that a minimum nitrogen content of 1.7 - 1.9 percent in the medium

* No. of grams of additional nitrogen required to decompose 100 gm. of material.

** No. of grams of nitrogen immobilized during the decomposition of 100 gm. of material.

was necessary for the aerobic release of nitrogen from rice straw; under anaerobic conditions 0.45 - 0.50 percent nitrogen was sufficient.

The reduction of the nitrogen factor and nitrogen equivalent has two important consequences. First, materials with relatively high C:N ratios may be used as nitrogenous manures; secondly, highly carbonaceous materials may be applied to submerged soils without any serious immobilization of nitrogen. But the results of one of the few studies on the use of straw as a manure for rice appear to run counter to these deductions. Jones (123) reported that rice straw at the rate of one and a half tons to the acre caused an eight percent decrease in yield -- a decrease which could be offset by the application of ammonium sulfate. He attributed the reduction in yield to immobilization of nitrogen by the organisms decomposing the straw. An alternative explanation is possible. The Stockton Clay Adobe Soil on which this experiment was conducted may have carried an appreciable charge of nitrate, part of which would normally have functioned as a source of nitrogen to the crop. In the presence of straw and the prevailing anaerobic conditions this source of nitrogen was probably lost by denitrification. Hence the response to ammonium sulfate.

Although the C:N ratio is relatively unimportant from the point of view of nitrogen immobilization it does have a marked influence on the rate of release of ammonia as the figures of Joachim and Kandiah (117) and of Mitsui (161) indicate. According to some of Mitsui's figures, peak ammonification was reached two weeks after incubation in flooded soil for all materials with a C:N ratio less than 9.1; the percentage of ammonia released during this period decreased from 80 percent for soybean cake with a C:N ratio of 5.3 to 40 percent for some alga matter with a C:N ratio of 9.1; peak ammonification for materials with C:N ratios wider than 9.1 was delayed progressively as C:N ratio increased.

Submergence of the soil modifies the process of ammonification in another way -- the process is rendered more sensitive to pH.

Under aerobic conditions, ammonification is accomplished by several groups of organisms each with its optimum pH range. For this reason ammonification in well drained soils is not markedly affected by pH within the pH range of normal soils. In a submerged soil the population is wholly bacterial and probably limited to a few types that operate most efficiently within a narrow range close to, and on the alkaline side of, neutrality. Ammonification in submerged soils should therefore be favored by a reaction slightly above neutral.

This aspect of nitrogen transformations in submerged soils had received no attention till in recent years workers in Japan began their enquiries into the age-old Japanese practice of liming rice soils. Mitsui (161) reports: "Curiously the Japanese farmers have laid much more importance to the application of lime to paddy rice field than to the upland." On the premise that rice was an acid tolerant plant they looked for some indirect effect of high pH in their search for an

explanation of the benefits of liming. They believed they had found the solution to the problem when they discovered that ammonification was more rapid at high pH values. Mitsui (161) concluded from laboratory studies that the increase in rate of ammonification became appreciable only above a pH value of 8.5. To obtain this high pH calcium carbonate was useless and according to Mitsui (161), calcium oxide had to be used. On the basis of Harada's finding that the alkali-soluble fraction of soil organic matter was more readily ammonified, Mitsui ventured to suggest that calcium hydroxide peptized soil organic matter and rendered it easier to decompose. This explanation is open to two criticisms. First, it is unlikely that even calcium oxide would raise the pH of a submerged soil to the high value of 8.5, except perhaps for a brief initial period, because of the high carbon dioxide tension in a submerged soil. Secondly, even if calcium hydroxide were to persist in the soil it is doubtful whether the hydroxide of a divalent metal could act as a peptizing agent. An alternative explanation is that the slight increase in pH, which calcium hydroxide would undoubtedly have caused, favored the activities of anaerobic bacteria and thus increased ammonification.

In recent years an additional feature of ammonification in submerged soils has received wide attention in Japan. It is the beneficial effect of drying a wet paddy soil on the process of ammonification after reflooding.

The beneficial effects on rice production of drying wet paddy soils between successive rice crops had long been known in Japan -- so much so that, according to Mitsui (161) "farmers often have obtained dried mud from lakes, rivers, ditches or irrigation canals and applied it to their fields." Experiments were started in many parts of Japan to determine the scientific basis of this widespread practice. The conclusion which emerged from these studies was that drying of the furrow slice prior to flooding resulted in an increased ammonification when the soil was submerged. According to Shioiri and Tanada (213) the increase in ammonia production due to pre-drying alone may be as high as 20 Kg. nitrogen per hectare. Japanese workers have attributed this increase in ammonification to the effect of partial sterilization of the soil during drying. An alternative explanation is possible.

In a submerged soil the decomposition of organic matter is slow because the organisms which effect this change operate at the low level of fermentation energy. When the soil becomes aerobic as a result of drying these organisms (anaerobic bacteria) will be replaced by a far more vigorous microflora of which fungi are probably the most active. Now fungi not only decompose organic matter efficiently but also synthesize considerable amounts of cell substance. Further, any small amount of ammonia they release will be seized upon by nitrifying bacteria and converted into nitrate. The results of drying, then, is the production of readily decomposable protein and nitrates. On submergence of a pre-dried soil, ammonification should proceed faster than in a continuously submerged soil because of the supply of easily decomposable organic matter, chiefly fungal tissue; secondly, the presence of nitrate permits the facultative anaerobes to participate in the decomposition. The lower

C:N of the substrate combined with the higher activity of facultative anaerobes compared with strict anaerobes will ensure rapid ammonification.

Further elaboration of the effects of drying on ammonification under submerged conditions is possible. Okuda (175) reported that when a pre-dried soil was submerged not only was ammonification more efficient but the redox potential too remained higher than for a continuously submerged soil. Shioiri and Tanada (213) confirm this. A high redox potential implies a low concentration of the reduced products, Fe^{+2} , Mn^{+2} and the virtual absence of S^0 . Could a high concentration of reduced products be injurious even to anaerobic bacteria? This is a question which merits investigation.

2.36 The Anaerobic Decomposition of Organic Matter

The decomposition of organic matter in a submerged soil differs from that in a well drained soil in two respects: (i) it is slower; (ii) the end products are different.

In a well drained soil decomposition of plant residues is brought about by a wide group of microorganisms assisted by the macro-fauna of the soil. Owing to the high energy release associated with the aerobic respiration of these organisms, decomposition of substrate and synthesis of cell substance proceeds at a rapid rate. The bulk of the added organic matter disappears as carbon dioxide leaving a residue of resistant material, chiefly altered lignin. Also there is a heavy demand on the nutritional elements, especially nitrogen. Under the anaerobic conditions that prevail in a submerged soil, on the other hand, the decomposition of organic matter is almost entirely the work of anaerobic bacteria with some assistance from the facultative anaerobes if nitrate is present to act as hydrogen acceptor in their respiration. Since anaerobic bacteria operate at a much lower energy level the processes of both decomposition and assimilation are much slower in a submerged soil than in a well drained soil. The accumulation of plant residues, as peat in bogs and marshes, is an excellent illustration of the slower rate of decomposition under anaerobic conditions than that in an aerobic environment. Laboratory studies bring out even more clearly the retarding effect of anaerobic conditions on decomposition.

Tenney and Waksman (234) studied the decomposition of a variety of plant materials under aerobic and anaerobic conditions. Their figures show that (i) with all the plant materials used anaerobic decomposition was slower than aerobic decomposition, (ii) the difference in decomposition rate was more pronounced in the case of the more resistant materials.

In the case of corn stalks "rich in water soluble substances including reducing sugars and nitrogen compounds" the loss by decomposition after four weeks incubation at 25-28°C was only 20 percent under

anaerobic conditions compared with the aerobic loss of 38 percent. The difference was more marked for the individual constituents. While the complex polysaccharides decomposed twice as fast under aerobic as under anaerobic conditions during the first four weeks, the lignin was hardly attacked in either case. But 20.6 percent of the lignin had disappeared at the end of 68 days compared with the anaerobic loss of only 7.7 percent at the end of 135 days. Even after a year only a third of the lignin was lost in the anaerobic decomposition.

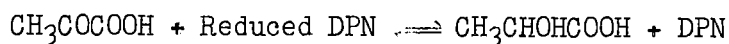
Rye straw, with its lower content of soluble carbohydrates and higher lignin content than the corn stalks, decomposed more slowly than the corn stalks under both aerobic and anaerobic conditions. Seventeen percent of the rye straw was decomposed in 66 days in the aerobic system and 7 percent in 84 days in the anaerobic system. The variation in sampling times render close comparisons difficult but it is clear the difference between aerobic and anaerobic decomposition rates is wider in the case of the more resistant rye straw than with corn stalks. This effect is brought out even more clearly in the decomposition of mature oak leaves. Under aerobic conditions 40 percent was decomposed in 286 days; the anaerobic decomposition rate was only about a fourth of this.

Even a high nitrogen content does not ensure rapid decomposition under anaerobic conditions. The figures for the decomposition of alfalfa show that under aerobic conditions decomposition was rapid and the nitrogen liberated lost as ammonia; under anaerobic conditions only 45 percent of the total material was lost even after 498 days and the nitrogen was largely preserved.

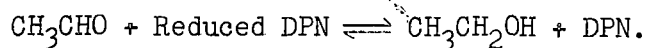
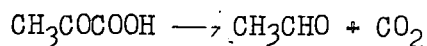
Acharya (1, 2, 3) and also Sircar and co-workers (217, 218) working with young and mature rice straw confirmed the findings of Tenney and Waksman and, in addition, stressed the low nitrogen requirement of the anaerobic decomposition process.

The most striking difference between the aerobic and anaerobic decomposition of organic matter lies in the nature of the end products. In a normal well drained soil the end products are mainly carbon dioxide, nitrate, sulfate and resistant residues. The products of organic matter decomposition in a submerged soil are chiefly carbon dioxide, methane, hydrogen, and organic acids derived chiefly from the carbohydrates and ammonia, amines, mercaptans and hydrogen sulfide from the proteins, and resistant residues.

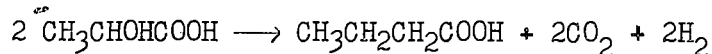
Carbohydrate metabolism is probably the same under both aerobic and anaerobic conditions till the formation of pyruvic acid as the end product of glycolysis. In a well drained soil the pyruvic acid, together with some of the carboxylic acids produced during the deamination of amino acids, is probably oxidized to carbon dioxide through the Krebs cycle, the H^+ ions and electrons produced being brought into union with atmospheric oxygen through the mediation of the terminal oxidases. At the low oxygen tension of a submerged soil the terminal respiration is suppressed so that pyruvic acid and the reduced DPN formed during glycolysis would tend to accumulate. But what apparently happens is that pyruvic acid is (i) reduced to lactic acid by the reduced DPN:



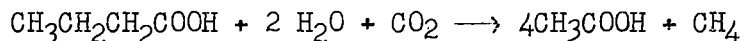
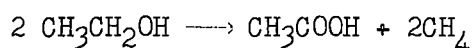
(ii) decarboxylated to acetaldehyde which in turn is reduced to alcohol:



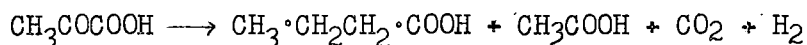
It is not necessary to invoke any specific organisms for these reactions for they are common features of anaerobic respiration. The products of these reactions may then undergo transformations in which specific bacteria are probably involved. Thus B. fossicularum may be responsible for the change:



While B. methanigenes probably converts alcohol and butyric acid into acetic acid and methane:



Clostridium Butyricum may act on pyruvic acid itself producing butyric and acetic acids (*).



Of these products, only lactic acid, acetic acid, butyric acid, methane and hydrogen have been shown to the present in appreciable amounts during the anaerobic decomposition of organic matter.

Subrahmanyam (229) studied the decomposition of diverse carbohydrates in water-logged soils under laboratory conditions. He noted that lactic acid was the first acid to appear but it decomposed readily forming acetic and butyric acids. In the decomposition of glucose he observed that lactic acid increased till the third day and then began to decrease while acetic and butyric acids increased till the fifteenth day after which they, too, decreased. The decomposition of lactic acid was favored by the presence of calcium carbonate.

Acharya (1) inoculated rice straw with soil and followed the decomposition under anaerobic conditions. He observed that the first phase of the decomposition was the rapid formation of organic acids. The second stage was the decomposition of the organic acids with the

* Barnett, A. J. G., Silage Fermentation, p. 101. Academic Press, 1954.

formation of methane and was more sensitive to acidity than the first. The products of the decomposition were acetic acid, butyric acid, carbon dioxide, methane and negligibly small amounts of hydrogen. In the absence of neutralizing agents he obtained as much as 20 gm. acid from 100 gm. straw. The ratio of methane to carbon dioxide was unity during the successive stages of the decomposition.

In further experiments Acharya (2, 3) studied the effect of temperature, pH and aeration on the course of the decomposition. Maximum decomposition as judged by loss of dry weight was observed at 30-35°C. Outside this range there was an accumulation of acids and a retardation of gas production. The initial stage of the fermentation was found to be more acid tolerant than the gas formation stage. Maximum loss of dry matter was observed at pH 8. Above and below this pH acids accumulated and gas formation was retarded. Mild aeration hastened the rate of decomposition and altered its course: smaller amounts of methane and organic acids were formed but carbon dioxide and hydrogen production increased.

Acharya's observations on the composition of the gaseous products are in agreement with the findings of previous workers (29, 31, 171). A curious feature is the very low proportion of hydrogen. Buruff and Buswell (29, 31) gave 3.5 percent and 1.7 percent for the concentration of hydrogen in gaseous products of two separate anaerobic fermentations of corn stalks. Nelson and co-workers (171) reported the still lower figure, 1.1 percent for a fermentation of wheat straw.

These observations assume some significance in the light of the behavior of the enzyme hydrogenase discovered by Stephenson and Stickland in 1931. This widespread enzyme reduces a number of one-carbon compounds, including carbon dioxide, to methane. It is remarkable that Harrison (92) forty years ago concluded from his study of the gases of swamp rice soils in India that bacterial reduction of carbon dioxide to methane by hydrogen took place in paddy soils. In fact he stated categorically: "carbon dioxide and hydrogen cannot as a matter of fact persist in association in paddy soils."

No review of the decomposition of organic matter is complete without a reference to the classic researches of Harrison and Aiyer into the gaseous products of the decomposition of organic matter in paddy fields. In a series of brilliant and exhaustive investigations into the composition of the gases of swamp rice soils Harrison and Aiyer (4, 92, 93, 94, 95, 96), forty years ago elucidated the essential features of the transformations of the methane, carbon dioxide and hydrogen in submerged soils. In this field, despite the lapse of forty years, their work stands unsurpassed for the boldness of their ideas, the high technical standards and thoroughness of their investigation and the facts they elucidated though their theory that these transformations were responsible for the aeration of rice roots must be considered erroneous.

Harrison and Aiyer noted that green manuring of paddy soils led to the production of large quantities of methane, with smaller

amounts of nitrogen, carbon dioxide, and hydrogen in the soil. But the gas that was evolved at the surface was found to be practically devoid of methane, hydrogen and carbon dioxide but rich in oxygen. They concluded that the gases produced in the soil underwent a profound transformation when they reached the film of algae, diatoms, and bacteria at the surface. Hydrogen and methane were oxidized by bacteria in the surface film to water and carbon dioxide respectively. The carbon dioxide was utilized by the algae with liberation of oxygen. They isolated from the algal film an organism capable of oxidizing hydrogen and Aiyer (4) identified the methane oxidizing bacterium as B. Fluorescens liquefaciens. They noted that green manuring stimulated the growth of the algal film and oxygen production and concluded: "one of the most important functions of green manuring lies in promoting an increased activity of the surface film which leads to greater aeration of the roots."

The anaerobic decomposition of proteins leads to the formation of ammonia, carboxylic acids, amines, mercaptans and hydrogen sulfide. The pathway of protein breakdown is probably the same for both aerobic and anaerobic decomposition till the formation of amino acids. Under aerobic conditions the amino acids are deaminated and the carbon residues probably oxidized via the Krebs cycle. In an anaerobic environment some of the products of deamination and decarboxylation may accumulate. Among these are the carboxylic acids, acetic, propionic, butyric, valeric and caproic acids. It is interesting to note that a substance with hormonal properties -- β -indole propionic acid -- is formed from tryptophane during anaerobic decomposition (251). The foul odor of submerged soils may be due to tetramethylene diamine from arginine; pentamethylene diamine from lysine; skatole from tryptophane; and mercaptans and hydrogen sulfide from cystine and methionine.

2.37 Increase in Solubility of Silica

Although submergence of the soil is believed to render silica more readily available to rice (222, 230, 231) there is no clear cut demonstration of the increase in solubility of silica as a result of submergence. Reed and Sturgis (199) reported that flooding caused an increase in the solubility of silica although their figures clearly indicate that silica was consistently lower in the solution from flooded soil than from the well drained. Mortimer's (166) findings, however, seem to indicate that there is an increase in soluble silica when lake muds undergo reduction. The close association between the release of silica and the reduction of the mud suggests that the release of silica into the water may be due (i) to the increase in pH, and (ii) the reduction of complexes of ferric hydroxide and silica.

2.38 The Chemical Profile of Submerged Soils

The reduced products present in a submerged soil are not distributed uniformly in the soil profile. Reference has already been made

to the presence of a superficial layer a few millimeters to a centimeter in thickness which can be distinguished from the layer below it by its color, its high redox potential and oxygen concentration and by the presence of the typical oxidized radicals Fe^{+3} , NO_3 , SO_4 , etc. The chemical and biochemical regime in this layer is apparently no different from that of an upland soil. Immediately below this and bounded by another oxidized zone below the plow sole lies the reduced zone of a submerged soil. This zone is characterized by a bluish-gray color, a low redox potential, a very low oxygen concentration and by the presence of the reduced products, Fe^{+2} , Mn^{+2} , S^{+1} , and the products of the anaerobic decomposition of organic matter.

The mobilization of iron, manganese and phosphate in the reduced layer has a profound effect on the development of a typical paddy soil profile. These soluble constituents are carried in the drainage water to the zone of high oxygen concentration below the plow sole and deposited there as concretions. This process leads to a gradual depletion of iron and manganese in the furrow slice and the development of a compact layer below the plow sole (138, 161, 214). In extreme cases, as in the old quartzose paddy soils of Japan, the deficiency of iron and manganese in the furrow slice leads to serious problems in rice production. Manganese deficiency (98, 214) and hydrogen sulfide injury (161, 214) are two factors that seriously reduce the productivity of these degraded paddy soils in Japan.

The presence of the thin oxidized layer at the surface of a submerged soil, too, is not without consequence. There are reports from Japan (161, 213) and also from India and Ceylon (45, 195) of the superiority of the deep placement of ammonium sulfate to surface application, in increasing rice yields. This is attributed to the preservation of the ammonium radical in the reduced layer for use by the crop in the case of deep application while surface applications are believed to lead to nitrification in the oxidized layer followed by loss of nitrate in the surface water and by denitrification when the nitrate enters the reduced zone. Phosphatic fertilizers, likewise, give better results when incorporated in the soil prior to flooding than when applied as a top dressing (161). When phosphate is mixed in the furrow slice the bulk of it will be present in the reduced layer where phosphate is rendered soluble. Surface applications lead to the fixation of phosphate chiefly as ferric phosphate in the oxidized layer. Egawa and co-workers (73) using radioactive phosphorus have demonstrated the accumulation of added phosphate in the surface layer in the case of normal paddy soils.

2.4 Biological Characteristics

The principal biological consequences of submerging a soil are the suppression of mesophytic vegetation, the reduction in bacterial and fungal numbers and the encouragement of the growth of algae. Of these, the suppression of mesophytic vegetation is so well

substantiated that it needs no elaboration. The reduction of bacterial and fungal numbers is also to be expected but it may be profitable to review the experimental evidence for the sake of the light it throws on the nature and extent of the process.

De and Bose (62) in a study of water-logged soils under laboratory conditions found that bacterial and fungal numbers were markedly reduced on water-logging and that the decrease became more pronounced with time. The effect was not permanent, for on letting the soils dry ammonifying and nitrifying activities were resumed. Takai (232) made the interesting observation that there was an increase in the number of aerobes immediately after water-logging but when the redox potential dropped below 0.1 volt the numbers decreased and fungi were rendered completely inactive. Stover and co-workers (226) found, in a field study, that flooding caused a fifty percent reduction in fungal numbers during the first thirty-five days; at the end of forty days eighty-five percent of the indigenous *Fusaria* were eradicated. On draining the fields there was an immediate increase in fungal numbers. In a later study Stover (225) noted that temperature had a marked effect on the survival of fungi in submerged soils and linked this effect with oxygen consumption and solubility. He also recognized the importance of the surface oxidized layer in fungal survival. Miller (158) and Tullis (237) emphasized the value of submergence in disease control. According to Miller, flooding of a peat soil resulted in the decomposition of sclerotia of *Sclerotinia sclerotiorum* within twenty days. Tullis found that seedling blight of rice could be checked and blast injury reduced by submergence of the soil. 1952

No aspect of the biology of submerged soils has in recent years received as much attention as the role of the blue-green algae in the nitrogen economy of rice soils. From the results of numerous investigations in India (64, 65, 216) and in Japan (91, 161, 245) the following facts emerge: (i) members of the genera *Nostoc*, *Anabaena*, *Oscillaria*, *Tolypothrix*, *Calothrix*, *Phoridium* are capable of fixing atmospheric nitrogen; (ii) some of these algae are present in most rice soils; (iii) some species may fix as much as 22.5 Kg per hectare of nitrogen in a season; (iv) the greater part of the nitrogen is not available for current needs of the crop; (v) nitrogen fixation is apparently increased by the presence of rice plants; and (vi) nitrogen fixation is favored by a slightly alkaline reaction and by the application of phosphates but retarded by the presence of nitrogenous fertilizers.

The fixation of nitrogen by algae is probably the most important long term benefit to rice accruing from submergence of the soil. The potentialities of the blue-green algae as a source of nitrogen may be gauged from the figure Arnon* has recently given for the nitrogen fixing capacity of *Anabaena cylindrica*. In laboratory cultures this alga fixed nitrogen at a rate corresponding to 480 lbs. of nitrogen per acre per month.

* Personal communication to Professor Bradfield, Cornell University, Ithaca, N. Y.

3. THE INFLUENCE OF SOME PROPERTIES OF SUBMERGED SOILS ON THE RICE PLANT

3.1 The Super-abundance of Water

The direct influence of the super-abundance of water on the rice plant may be dismissed as a matter of little consequence. In this connection, it is of interest to note that the transpiration ratio of rice is only slightly higher than that of many arable plants (35, 144, 239).

3.2 The Deficiency of Oxygen

The deficiency of oxygen in a submerged soil raises two questions of fundamental importance: (i) how does rice germinate and grow in a medium very low in oxygen, and (ii) has the low concentration of oxygen, *per se*, a beneficial effect on rice? The answers to these questions emerge from studies on the response of rice to oxygen tension and from anatomical studies of the rice plant.

The germination and growth of rice at low oxygen tensions has been the subject of numerous investigations during the past fifty years. The early experiments in Japan which were of a semi-quantitative character have been reviewed by Jones (121) and by Vlamis and Davis (242). These studies brought out two features of the germination of rice: first, rice is able to germinate at extremely low oxygen concentrations and secondly, the elongation of the plumule is favored and that of the radicle is retarded by low oxygen concentrations while high oxygen concentrations have the opposite effect. It is also of interest to note that of a wide variety of seeds tested, Hutchins (107) found that rice seeds germinated at the lowest oxygen pressure.

Recent quantitative studies have confirmed the early observations and thrown some light on the mechanism of this peculiar behavior of rice.

Vlamis and Davis (242) made a quantitative study of the germination, growth, and respiration of rice and barley at low oxygen pressures. They noted that the percentage of rice seed germinated was independent of oxygen pressure over the entire range studied (0.2 - 21 percent) although the percentage of barley seed germinated decreased sharply below an oxygen pressure of 9.5 percent. They also confirmed the retardation of shoot growth of rice seedlings by high oxygen pressures. According to their figures shoot growth was least at 21 percent oxygen pressure, and maximum at 3 percent oxygen pressure; even below 3 percent oxygen pressure shoot growth was higher than at 21 percent oxygen pressure. In sharp contrast to the behavior of the rice seedlings,

barley seedlings showed a marked decline in shoot growth below 9.5 percent oxygen pressure. Root growth of both rice and barley seedlings was markedly reduced below this oxygen pressure. Another significant observation these workers made was that carbon dioxide production by rice seedlings decreased much less rapidly than in the case of the barley seedlings as oxygen pressure was reduced.

In a similar comparative study of wheat and rice, Taylor (233) confirmed the remarkable ability of rice to germinate and grow in an environment very low in oxygen. He observed a marked decrease in total germination of wheat seeds below 5 percent oxygen pressure and no germination at all in the absence of oxygen. But total germination of rice was the same even in the absence of oxygen although the rate of germination was slightly reduced. Rice seedlings exhibited a similar but less marked insensitivity to oxygen pressure. Growth of both rice and wheat seedlings declined (the wheat seedlings more rapidly) as oxygen pressure fell but even at 0.3 percent oxygen rice seedlings made 15 percent of their growth at 21 percent oxygen pressure. The inhibition of root growth by low oxygen tension was also confirmed.

In an attempt to find the physiological reason for the curious behavior of rice, Taylor studied respiration (as measured by oxygen uptake) and growth of wheat and rice seedlings over a range of oxygen tensions. He observed that with decrease in oxygen pressure both oxygen uptake and growth declined rapidly in roughly parallel fashion for wheat. In the case of the rice seedlings growth remained at a high level in spite of rapid and continuous decrease in oxygen uptake as oxygen pressure was lowered. Taylor therefore concluded that rice had a fermentation system which functioned strongly enough to compensate for decreased aerobic respiration. Additional evidence in support of this view is summarized below.

Erygin (76) determined the respiration coefficients (CO_2/O_2) of seeds germinating under water. His figures were 1.40 for barley, 3.86 for upland rice, and 4.50 for lowland rice. Anaerobic respiration is clearly greatest in lowland rice. The observation of Vlamis and Davis (242) that carbon dioxide production decreased much less rapidly for rice seedlings than for barley seedlings as oxygen pressure was reduced again points to higher anaerobic respiration by rice. The peculiar behavior of rice noted by Vlamis and Davis (243) in their study of accumulation of salts by excised rice roots suggests that the same mechanism is at work again. They found that below an oxygen pressure of one percent tomato and barley roots lost large amounts of potassium. They noted that the loss from rice was "very slight," and remarked: "the significance of this remains to be determined." Recently Okajima and Kimura (173) have adduced further evidence for the presence of active anaerobic respiration in rice from their studies on the influence of oxygen and respiratory inhibitors on the exudation of sap by decapitated rice seedlings.

The presence of a highly developed system of anaerobic respiration probably accounts for the ability of rice to germinate and grow at

low oxygen pressures but it does not explain the stimulation of shoot elongation and retardation of root elongation by low oxygen pressures. Yamada (252) has recently attempted to give a partial solution to this problem. He concluded from his studies on the influence of indole acetic acid on decapitated rice coleoptiles grown floating and submerged in water that the superior growth of the rice coleoptile under water was probably due to a lower capacity of the tissue to destroy auxin at the low oxygen concentration in a submerged milieu.

In the light of these laboratory studies and of the profile of a submerged soil the results of field experiments on the germination of rice become clearly intelligible.

Jones (121) found that rice sown on the surface of the soil, half inch and one inch deep and then continuously submerged produced 78, 20 and 2.6 percent of seedlings respectively. No seedlings were obtained below one and a half inches. In pot experiments seedlings were obtained even below this depth when oxygen was passed through the soil. Jones concluded that below a depth of half an inch there was insufficient oxygen to initiate the development of the radicle. Nelson's (170) findings were similar. He noted that when rice was sown on the surface and then irrigated it came to a full stand; when rice was drilled and irrigated the stand was poor. Jones (121) also drew attention to the morphological differences between rice seedlings from seed germinated under continuous submergence and from seed drilled but alternately flooded and drained. Seedlings from the continuously submerged seed had long, narrow, delicate leaves and poorly developed roots and were not properly anchored while the seedlings from drilled rice alternately flooded and drained had short, wide deep green leaves and an extensive root system well anchored in the soil.

It would appear from the experiments cited above that the ability of rice to germinate and grow in an environment low in oxygen, at least in the initial stages, is due to an efficient system of anaerobic respiration. The next question is whether this explanation is applicable to those parts of the plant which continue to grow in an environment low in oxygen beyond the initial stage. The findings of Vlamis and Davis (243) give a negative answer to this question.

Vlamis and Davis found that excised rice roots from five-week old seedlings behaved very much like the excised roots of barley and tomato in their response to changes in oxygen concentration. For all three kinds of roots accumulation of bromide and potassium increased sharply in the range 0.2-3 percent oxygen tension and became practically independent of oxygen tension beyond 3 percent. Respiration showed a somewhat similar response. Since there were no marked differences in oxygen sensitivity by the excised roots Vlamis and Davis studied the behavior of the roots of these three plants with the shoot system attached. They made the remarkable discovery that rice roots of intact plants could carry on metabolic processes under the anaerobic conditions that retarded these processes considerably in intact barley roots

and inhibited them in intact tomato roots. They concluded oxygen was transported from shoot to roots in the case of rice and barley plants.

It had long been assumed that the submerged parts of aquatic and marsh plants derive their oxygen supply from the aerial parts. The presence of aerenchyma in the tissues of these plants had been postulated but experimental evidence has been supplied only for a small number of plants and that only in recent years (52). In the case of rice the situation was even worse for despite its adaptation to a semi-aquatic habitat it was believed to have a root anatomy characteristic of upland plants. In fact Sethi (211) stated emphatically: "Anatomical observations show that the rice plant is not an aquatic plant. Aeration is absolutely *necessary for the healthy development of the plant.*" In view of the uncertainty about the presence of the anatomical features required for oxygen transport from shoot to roots it is necessary to review briefly the relevant aspects of the anatomy of rice roots.

According to Sethi (211) the root system of rice after a fortnight's growth consisted of two distinct types of roots: (i) bold, white, short, unbranched roots, of waxy appearance; (ii) long, thin, flaccid, light brown and much branched roots. The bold, white, waxy roots were devoid of air spaces and resembled the roots of upland plants. About six weeks from germination these roots began to branch and become weak and flaccid until at maturity all roots were thin, branched and flaccid. The old flaccid roots were impregnated with red coloring matter and large air spaces were present in the cortex. Since the white roots predominated during the greater part of the life of the plant Sethi concluded that aeration of the medium in which they grew was necessary for healthy growth.

Hector (99) describes the anatomy of the rice root in some detail but, like Sethi, reports the presence of air spaces only for the older roots.

The observations of Juliano and Aldama (126) are different in that they include the presence of intercellular spaces even in young roots. The relevant portion of the description Juliano and Aldama gave of the anatomy of the rice root is reproduced. "The rest of the cortex is composed of large rounded or hexagonal to rhomboidal cells which are arranged in rows, and these tend to become smaller inward. Between these cortical cells are found rhomboidal intercellular spaces. These cortical cells later disintegrate with the formation of large air spaces or chambers. These are separated by bands of degenerated and collapsed cortical cells leaving a single layer of cells intact below the sclerenchymatous cylinder and another layer above the endodermal cells. The linear rows of cortical cells separating the air chambers remain attached to these persistent layers of cells like the spokes of a wheel."

Juliano and Aldama (126) also reported the presence of large air channels in the leaves, the leaf bases and in the internodes of the stems.

The presence of air spaces in rice roots is not by itself a proof of the transportation of oxygen from the shoot system to the roots. The air spaces may be merely a consequence of the development of these roots in an anaerobic medium, for the presence of air space has been reported in corn and barley roots in non-aerated solutions. Beal (23) reported that cortex of aerated corn roots had cells of uniform size and showed no air spaces whereas non-aerated roots contained large air cavities separated by narrow strands of tissue. Bryant (40) found that the cortex of aerated barley roots consisted of uniform compact parenchyma with no conspicuous intercellular spaces while the cortical region of the non-aerated roots contained large air passages separated by narrow strands of parenchyma. McPhearson (154) noted that the production of air spaces in non-aerated corn roots was preceded by the deterioration and death of the protoplasm in groups of cells. During the deterioration the cells lost their rigidity and the walls crumpled and collapsed.

Conclusive proof of the flow of oxygen from the shoots to the roots of the rice plant comes from the brilliant researches of Van Raalte (192, 193) in Indonesia.

Van Raalte first determined the oxygen and carbon dioxide concentrations in the gas spaces of rice roots. He cut consecutive segments of rice roots under acidified glycerol and pressed the gas from the root segments into a micro gas-pipette. The gas analyses for two varieties are reproduced below.

Segment	Variety 1		Variety 2	
	CO ₂	O ₂	CO ₂	O ₂
tip	4.7	2.1	1.9	8.1
middle	6.9	4.9	3.2	8.4
base	6.1	9.0	2.8	14.0

These figures show that there is a gradient in oxygen concentration from the base to the tip of the root. The comparatively high oxygen concentration was maintained even when the roots were placed in a highly reduced medium. Van Raalte concluded from this that the oxygen in the roots did not come from the external solution. He naturally inferred that it came from the aerial part of the plant and proceeded to trace its course. He found that ringing or ligaturing the roots reduced the oxygen concentration in the tip, and concluded that oxygen was transported in the cortex of the roots. In a series of further experiments he proved that the atmosphere was the real source of the oxygen found in the roots. The evidence was: (i) more oxygen was found in the roots of a decapitated plant than in roots of the intact plant, and (ii) sealing the cut surface reduced the oxygen concentration in the roots. Not satisfied with these clear indications of the flow of oxygen from shoot to roots Van Raalte proceeded to show the continuity of the air channels in the roots

and aerial parts. He cut a plant 10 cm. above the roots, attached it to a pump and placed the roots with their tips cut in Chinese ink. On applying suction the ink appeared in the air chambers of the leaf bases and stem. Microtome and hand sections of these tissues showed that the intercellular spaces of these tissues constituted the channels through which oxygen was transported.

Van Raalte thus established beyond any doubt that the transport of oxygen from the shoots to the roots enabled the roots to function aerobically in an anaerobic environment.

In a further experiment Van Raalte (193) showed that the influence of oxygen is not limited to the root cells: it reaches also the soil. The thin layer of brown ferric oxide around rice roots noted by earlier workers, he attributed to the diffusion of oxygen from the roots. He proved the diffusion of oxygen from the roots by showing the marked increase in redox potential that took place when the roots of an intact rice plant were placed in a highly reduced medium. He further assessed the oxidizing capacity of a two-month old rice plant as the equivalent of 1-3 mg. of oxygen per day. He also drew attention to the practical significance of this oxygen diffusion: the oxidized state of the immediate environment of rice roots prevents the influx of reduced products into the roots and enables aerobes to function in the immediate vicinity of the roots. Subsequent simple experiments by Japanese workers have confirmed many of Van Raalte's findings.

Mitsui (161) furnishes an illustration of the diffusion of oxygen. He transferred a rice seedling from a reduced atmosphere to an agar medium containing leuco-methylene blue. Within a few hours the color of methylene blue was visible in the rhizosphere. The color was well developed only in the region of the root tip of older roots but along the entire length of very young roots. Mitsui inferred from these observations that in a paddy soil young roots remained white because the greater diffusion of oxygen from them caused the deposition of ferric oxide beyond the root surface; in the case of old roots, where diffusion of oxygen was retarded by the presence of suberin and lignin, deposition of ferric oxide took place on the root surface itself giving it a reddish brown color.

Kumada (143) using luminous bacteria gave further proof of the diffusion of oxygen from rice roots. Yamada and Iyama (253) found carbon dioxide and oxygen contents of 4.6 c.c. and 7.4 c.c. per gm. fresh weight of the roots and noted that oxygen content decreased at heading time.

The experiments thus far reviewed indicate that rice has two adaptive mechanisms which enable it to thrive in a submerged soil: a highly developed system of anaerobic respiration, at least in the early phases, and the transport of oxygen from shoot to root in the later stages. Recently Alberda (7) has adduced evidence for the operation of a third mechanism -- the transport of oxygen from the surface to the roots below by a specialized type of superficial roots.

Alberda drew attention to references in the literature to the mat of fine superficial roots developed by rice plants about the end of the tillering period. He showed that the appearance of these roots coincided with the time when oxygen concentration in the roots was beginning to decrease, presumably due to restriction of oxygen transport from shoot to roots. This restriction, Alberda attributed to the lengthening of the internodes. The slower rate of oxygen diffusion from shoots to roots was, according to Alberda, compensated for by the diffusion of oxygen from the fine superficial roots. When the development of these roots was prevented the redox potential of the soil was lowered and the root system in the soil appeared poor. Some of Sato's (208) observations on the changes in oxygen concentration in the culture solution during the growth and maturity of rice plants lend support to Alberda's view.

It is clear from the evidence cited above that rice roots do not depend on their environment for their oxygen supply. Strangely enough the theory which was accepted most widely and, despite its patent inconsistencies, is still being quoted in textbooks (89, 204) and in articles (241) is the very antithesis of this. It is Harrison and Aiyer's (93) theory of the aeration of rice roots by the slow downward movement of oxygenated water past them.

Reference has already been made to Harrison and Aiyer's observations on the transformations of methane, hydrogen and carbon dioxide at the surface film of algae and bacteria in paddy soils. The most important result of these transformations was the enrichment of the supernatant water in a paddy soil, with oxygen. According to Harrison and Aiyer, in undrained soils this oxygenated water did not penetrate into the soil and consequently the roots were congested near the surface of the soil and the crop suffered. In soils with drainage the oxygenated water penetrated into the soil and enabled the roots to function at greater depths. This resulted in a more vigorous crop. Excessive drainage was not beneficial because it prevented the formation of the surface film which was responsible for oxygenation of the water while aeration by atmospheric oxygen was not as effective as aeration by dissolved oxygen. Green manures promoted aeration because they generated methane which was oxidized at the surface to carbon dioxide which in turn was assimilated by the algae with liberation of oxygen into the irrigation water.

There are two glaring inconsistencies in this theory. First, how can methane and hydrogen, typical products of the anaerobic decomposition of organic matter, be formed in a medium perfused with oxygenated water? Secondly, if the benefits of drainage derive from the aeration of the roots why is aeration by atmospheric oxygen under well drained conditions not as effective as aeration by oxygen dissolved in the water?

The deficiency of oxygen per se in a submerged soil is not injurious to rice. Could normal concentrations of oxygen be harmful to rice? If this were so it could be one of the reasons for the better growth

of rice in submerged soils. The results of the experiments of Vlamis and Davis (243) and Lin (147) answer this question in the negative.

Vlamis and Davis grew rice seedlings for six weeks in culture solutions with the following gas treatments: (i) no gas bubbled; (ii) nitrogen bubbled, and, (iii) air bubbled. There were no significant differences in the fresh weight of shoots or roots, and potassium accumulated. They noticed a slight discoloration of the roots when air was bubbled -- a discoloration due probably to deposition of ferric hydroxide. Lin found that, in a wide variety of culture solutions, growth of rice plants was unaffected by oxygen concentrations ranging from 0.2 to 20.8 percent in the gas used for aerating the culture solutions. These experiments show that oxygen concentrations up to 21 percent have no deleterious effect on rice.

The evidence is clear that a deficiency of oxygen in a submerged soil has no injurious or beneficial effect on rice.

3.3 Excess of Carbon Dioxide

High concentrations of carbon dioxide are injurious to plants.

Kramer (141) observed a rapid reduction in water absorption by sunflower and tomato seedlings, the roots of which were exposed to high concentrations of carbon dioxide and suggested that it was probably due to decreased permeability of the protoplasmic membrane.

Leonard and Pinckard (145) reported that a carbon dioxide tension of 30 percent reduced root growth of cotton without affecting shoot growth; a tension of 45 percent reduced both shoot and root growth and a tension of 60 percent caused wilting of the plants.

Vlamis and Davis and also Chang and Loomis have shown that rice responds similarly.

Vlamis and Davis (243) found that while bubbling nitrogen through the culture solutions in which tomato, barley and rice seedlings were grown markedly reduced the growth of tomato, appreciably reduced the growth of barley and had no effect on the growth and other metabolic processes of rice, bubbling carbon dioxide was "immediately lethal to all plants." In experiments with barley they noted that a carbon dioxide tension of 20-30 percent was toxic to the plants even when the residual 70-80 percent was all oxygen.

Chang and Loomis (46) noted that bubbling carbon dioxide through water cultures of wheat, maize, and rice, for ten minutes each hour, reduced water absorption 14-50 percent and retarded the absorption of nutrients in the order $K > N > P > Ca > Mg$. They showed that the effect was not due to acidity for it was more pronounced with carbon dioxide than with sulfuric acid added in an amount to give the same degree

of acidity. They also concluded from a survey of the literature that carbon dioxide concentrations of 15-20 percent may be lethal to some plants.

The usual concentration of carbon dioxide in paddy soils is fortunately below this toxic level. According to Harrison and Aiyer (93) the concentration of carbon dioxide in the paddy soils they examined ranged from 1-20 percent with a mean of 5 percent. The possibility cannot be excluded, however, of concentrations of carbon dioxide much in excess of 20 percent during the initial stages of the decomposition of organic matter in paddy soils. Janssen and Metzger's (112) failure to obtain growth of rice seedlings in submerged soil manured with vetch unless planting was delayed two weeks may have been due, in part, to carbon dioxide toxicity. In the later stages of organic matter decomposition in paddy soils two factors tend to keep the carbon dioxide tension low: (i) the diluting effect of methane, which according to Acharya (1) is not produced in large quantities in the early stages and (ii) to the reduction of carbon dioxide by hydrogen as indicated by Harrison (92).

3.4 Increase in pH

The increase in pH brought about by submergence of the soil probably has no appreciable direct influence on the rice plant. But there are strong reasons for supposing that the actual pH, especially the pH level at submergence or the early stages of submergence, will have a marked influence on the crop through its effect on the chemical and biochemical processes in the soil.

The influence of pH on the biochemical changes and the chemical equilibria in a submerged soil has already been discussed, but in order to assess the effect of pH on the crop it is necessary to recapitulate the significant aspects of the biochemical and chemical responses to pH.

A low pH retards denitrification, sulfate reduction and ammonification but favors the accumulation of organic acids. A pH slightly above neutral has the opposite effect. Since nitrates, sulfates and organic acids do not in any case persist for an appreciable length of time the main significant effect of low pH is to reduce the supply of available nitrogen for the needs of the crop. For this reason alone a pH slightly above neutrality should be better for rice than a low pH. Chemical considerations give added support to this view.

The main effect of low pH is to increase the concentration of Fe^{+2} and Mn^{+2} ions in the soil solution. Since considerable amounts of Fe^{+2} and Mn^{+2} may be present in solution even at a pH value near neutrality, under the anaerobic conditions of a submerged soil any deleterious effect high concentrations of Fe^{+2} and Mn^{+2} may have on rice will be accentuated at low pH values.

Theory thus suggests that a low pH should be unfavorable to rice. Practical experience provides a striking confirmation of this.

According to Mitsui (161) liming of acid rice soils is a common practice in Japan. What is more, "Japanese farmers have laid more importance to the application of lime to the paddy rice field than to the upland." Laboratory and field studies have confirmed the soundness of this practice. Chang and Huang (47) report from Formosa that in more than 200 field plot experiments on acid soils of Taiwan (pH 4.0-6.0) ninety-five percent of the experiments showed increased yields of rice when three tons per hectare of lime was applied. In another series of experiments, also in Formosa, Chang and Puh (48) found that on acid soils (pH 4.5-6.3) the response to a basal dressing of 80 Kg per hectare of fertilizer increased progressively as the rate of lime application was increased from one ton to 3 tons per hectare. Sethi (212) reported that in Malabar soils known to be deficient in lime gave consistent increases in yield with increased application of lime. Finally, Ignatieff (109) reports without comment the responses of rice to liming in at least seven different countries.

The only direct references to ill effects of low pH on rice are those by Kapp (129) and Kobayashi (137).

3.5 Low Redox Potential

Gillespie (85) suggested that the low redox potential per se may be a factor of ecological significance, but it was left to Pearsall (179) to provide the experimental verification. Pearsall was able to show an association of the distribution of natural types of woodland vegetation in Northern England with soil properties which could be characterized by redox potential and pH. There was no such success when Sturgis (227) attempted to use redox potential as an index of the productivity of rice soils under greenhouse conditions. Apparently this discouraged further experiments on these lines for there is little information in the literature on the influence of redox potential on the rice plant.

In the absence of experimental data, a little theorizing would not be out of place.

The redox potential per se could have no effect on the rice plant in view of the oxidized state of the immediate environment healthy to rice roots. But the reducing intensity, as pointed out earlier, can have a marked effect on the concentration of substances which can have an injurious effect on rice if they are present in excess. The situation is aggravated when a low redox potential is combined with a low pH though, of course, a lowering in redox potential is invariably accompanied by an increase in pH. Under these circumstances a rice plant would be deluged with reduced products especially Fe^{+2} and Mn^{+2} but for the astonishing ability of the very parts of the root system -- young roots and the tips of the older roots -- concerned in active accumulation of ions, to exude oxygen and maintain an oxidized environment. No elaborate calculations are necessary to show that there is a limit even to this protective device. This limit is most likely to be reached when an acid soil with a high content of iron and manganese attains a low redox potential.

3.6 Increase in Solubility of Iron

The greater solubility of iron in a submerged soil than in an upland soil is within limits beneficial to rice for there is abundant evidence that the iron requirement of rice is higher than that of upland plants.

Gile and Carero (83) were the first to stress the importance of iron in the nutrition of the rice plant. They noted an unusual sensitivity of rice to the reaction of the culture solution when ferrous sulfate, ferric chloride and colloidal ferric hydroxide were used as the source of iron. These substances caused chlorosis in neutral and alkaline solutions but not in acid solutions. The percentage of iron in the plants was 50 percent higher in the acid than in the neutral or alkaline treatments. The behavior of ferric tartrate was different: it caused no chlorosis even in alkaline solution. They also noted that growth improved as the concentration of iron in the solution was increased from 2 p.p.m. to 8 p.p.m. The same workers (84), a few years later, found that chlorosis of upland rice grown on calcareous soil was cured by submergence of the soil and ascribed the effect to greater assimilation of iron by the plants.

Gericke's (86) studies on the nutrient requirements of rice in solution cultures bring out more clearly the unusual iron requirements of rice. He found that addition of iron to nutrient solutions needed to be more frequent for young rice seedlings than for wheat, barley, rye and oats grown under the same conditions. Rice also required available iron in culture solutions longer than any other element barring nitrogen and potassium. The absence of iron in a fresh culture solution even after three months' growth in a complete culture solution caused the plants to become "progressively yellow, chlorotic and etiolated" and to cease growing. Iron supplied as citrate was available to rice but ferrous sulfate, ferric chloride and ferric phosphate became unavailable in nutrient solutions containing nitrate although iron in these compounds was available to wheat, barley, and oats grown in the same solutions. Rice suffered no ill effects from the use of these sources of iron when ammonium salts were used instead of nitrates.

Thelin and Beaumont (235) noted the same unusual demand of rice for iron in their water-culture studies on rice and wheat.

Lin (147) confirmed the observation of previous workers that rice grown in nutrient solutions with nitrate as source of nitrogen developed chlorosis and pointed out that the symptoms were those of iron deficiency. Chlorosis was prevented by the simple expedient of adding a little sodium thioglycollate, a powerful complexing agent for iron, to the culture solution. Lin was the first to suggest that the better growth of rice in submerged soils than under upland conditions might be due to increased availability of iron.

The experiments cited above emphasize the abnormally high iron requirement of the rice plant but shed no light on the quantitative aspects

of the problem. Unfortunately, quantitative studies are very few and limited in scope. Further, the complex interactions especially among the heavy metal ions and the difficulty of assessing the amount of iron in true solution make it impossible to fix a critical or optimum level of iron for rice even in culture solutions. The findings reported below may therefore be taken merely as confirmation of the higher demand of iron by rice than by other crop plants.

Kapp (128) found that the green color and root growth of rice in culture solutions improved as the concentration of iron increased from 1 to 25 p.p.m. but at 50 p.p.m. there was a decline in growth and number of tillers. Aiyar (5) reported that the best results were obtained with an iron concentration of 32 p.p.m. Growth was good at 8 p.p.m. Below 2 p.p.m. deficiency symptoms appeared. Like Gericke, Aiyer emphasized the necessity of providing iron continuously through the period of growth.

The importance of iron in the nutrition of the rice plant suggests that one of the beneficial effects of submergence may be an increase in the supply of available iron. But important as iron is in the nutrition of rice the possibility of toxicity due to an excess cannot be excluded. Reference has already been made to Kapp's observation that iron in excess of 50 p.p.m. was harmful to rice. In a further study Kapp (129) reported that when the iron concentration was increased from 25 p.p.m. to 500 p.p.m. the weight of heads decreased 33 percent, straw yield 20 percent, and weight of roots 18 percent. Despite the obvious limitations of this study it indicates that iron in excessive amounts may be toxic to rice. There are indications that this may be true even under field conditions in spite of Aiyer's (5) gratuitous assertion that "An excess of iron is not known to be toxic to the rice crop."

Workers in India (94, 194) have reported that a moderate amount of drainage is beneficial to rice grown even under submerged conditions. In the absence of drainage roots were confined to the first few inches and growth and yield were adversely affected. They attributed this to defective aeration of the rice roots. In the light of recent knowledge regarding the oxygen supply of rice roots their observation demands a different explanation. Could the poor growth of rice in submerged soils with no drainage be due to a toxic accumulation of reduced products? There is no direct evidence for this but certain facts that have been brought to light about a widespread physiological disease of rice strongly suggest that an excess of reduced products, especially iron, may be toxic to rice.

In recent years, a physiological disease of rice known as "mentek" in Indonesia, "penyakit merah" in Malaya, "browning disease" in Ceylon and under various local names in India and Burma has received increasing attention. Van der Vecht (240) has published an exhaustive report on "mentek" in Java and Johnston (125) has described in considerable detail three types of "penyakit merah" in Malaya, while Joachim (115, 116) has reported "browning disease" and its treatment in Ceylon. Also Aiyer (6) has described a disease with similar symptoms in Burma, and Sik (215),

in Hungary. The widespread occurrence of this disease and the magnitude of the losses due to it recently prompted the International Rice Commission to undertake a study of the problem on a cooperative basis.

It is still too early to refer to the physiological disturbances described under the various local names in widely separated areas as a single disease but the descriptions of the symptoms and of the modes of occurrence are so similar that they would appear to have a common cause.

The chief symptoms of the disease are: a stunting of growth; a reddish discoloration of the older leaves followed by a pronounced marginal scorch, curling, and death of the leaves; a damaged root system; and poor panicle and grain development. The symptoms are so much like those of potassium deficiency that they have in fact been attributed to it (6, 115, 116, 142). The disease is confined exclusively to low-land rice particularly in the plains (87, 240); it is associated with very poor drainage (87, 240); it appears when fields have been unduly long under water (87, 240); it is aggravated by unfavorable climatic conditions; the severity of the disease in a given locality varies from year to year. Common control measures in Java (87, 240) are delaying submergence and draining of the fields.

The close association of the disease with poor drainage at once suggests that the accumulation of reduced products may be responsible for the disease. Indeed, van der Elst as far back as 1914 concluded from his extensive knowledge of the rice crop under field conditions in Java: "The direct cause of the disease . . . is the withholding, and more particularly the withdrawal of oxygen from the root system by reducing substances." (240).

Owing to the unfortunate emphasis that van der Elst placed on the oxygen supply rather than on the effect of the reducing substances on the plant, his theory was superseded by Kuilman's idea that a poor root system coupled with potassium deficiency is responsible for the disease (142). More recently van der Vecht (240) has suggested that the nematode Randolpholus oryzae is the cause of mentek. But in all his wide survey of the mentek problem van der Vecht could muster only three reasons for the rejection of van der Elst's theory. They were: (i) rice fields kept submerged uninterruptedly suffered less from the disease than they did before; (ii) "in some areas rice fields which were almost continually irrigated were found to be only rarely attacked by the disease"; (iii) rice roots derive their oxygen supply from the aerial parts and are therefore not affected by oxygen deficiency in the soil. None of these objections is tenable against the view that the disease is due to toxicity of the reduced substances themselves, for duration of submergence is not the only factor that determines the extent of reduction. Further, the poor root system, on which Kuilman and van der Vecht placed so much emphasis as the cause of the disease may well be the result of injury due to high concentrations of reduced products.

It is strange that Dutch workers in Java with their century-old and wide acquaintance with the disease have not recognized the influence that a high concentration of reduced substances can have on the rice plant when workers (79, 215) in Hungary with their more limited experience have recently noted that "browning disease" of rice is associated with strong reductive processes in the soil.

The next problem is to decide which one or more of the reduced products is the chief toxic factor. All the available evidence suggests that it is iron.

First, in a highly reduced soil the content of reduced iron is normally far in excess of reduced manganese, an alternative candidate for the role of toxic factor. The lower solubility of ferrous hydroxide, carbonate and sulfide is no bar to the presence of large amounts of iron in solution because of the ease with which iron forms soluble complexes with the products of the anaerobic decomposition of organic matter.

Secondly, the symptoms of the disease are similar to certain symptoms associated with iron toxicity in other members of the Gramineae family. Hoffer (105) drew attention to nodal discolorations in young corn plants grown in nutrient solutions containing ferrous sulfate and indicated how the clogging of the sap conducting vessels led to injury to the root system and the foliage. He also reported the presence of large accumulations of iron in the nodal tissues of corn plants from an acid muck soil in which root rot had caused severe damage for years. Harvey, cited by Hartt (97), found that in corn grown in acid soil there may be a deposit of ferric oxide in the vascular tract sufficient to interfere with translocation and cause firing of the leaves. It is interesting to note that Aiyer (6) found brown streaks of iron oxide in the nodes of plants in which he induced chocolate colored patches on the leaves, leaf scorch, and root rot -- symptoms commonly associated with mentek -- by withholding potassium from the culture solution. Also Joachim (116) reported that leaves affected by the browning disease had a higher content of iron and a lower content of potassium than healthy leaves.

The close similarity of the symptoms of the disease to those of potassium deficiency and the amelioration of the symptoms by the application of potassic fertilizers also suggests that iron may be the toxic factor, for a close association has been observed between iron toxicity and potassium deficiency in other members of the Gramineae.

Hoffer (105) noted that the accumulation of iron in the nodes of corn plants cleared up when heavy applications of potassium were made. Hartt (97) in her exhaustive water-culture studies on sugar cane noted that the percentages of iron in the blades, stems and roots of plants deficient in potassium were higher than in the controls. The addition of potassium caused some of the iron that had accumulated in the roots and stems to pass into the blades. Hartt also drew attention to a controversy in Java about the cause of "Kalimati" disease of sugar cane.

Since the symptoms were very similar to those of potassium deficiency and were corrected by the addition of potassium, the disease was believed to be caused by potassium deficiency. The other view was that it was caused by ferrous iron and that the effect of potassium was to counteract the injurious action of iron. In view of the retarding action of nitrate on the reduction processes in the soil it is highly significant that the disease was absent when nitrate instead of ammonium was used as nitrogenous fertilizer. Noguchi and Sugawara (172) reported that similar symptoms on rice plants grown on a soil reported to be deficient in potassium were ameliorated when nitrate instead of ammonium was used as the source of nitrogen.

In the light of these observations, it is instructive to consider briefly the symptoms and the treatment of this physiological disease of rice associated with poor drainage. The discoloration and withering of the leaves and a damaged root system are the outstanding symptoms of the disease. These symptoms have been observed even in soils carrying over 0.2 m.e. per 100 gm. of exchangeable potassium (6). This excludes a deficiency of potassium in the environment as the causative agency. The accumulation of iron in the nodes and the roots of affected plants suggests (i) that the concentration of potassium in the plant is low, (ii) that the external iron concentration is high, for Rediske and Biddulph (196) using radioactive iron have shown that the mobility of iron in the tissues is reduced by a high external concentration of iron. The deficiency of potassium in the tissues probably retards protein synthesis while the clogging of the vascular tissues by deposits of iron oxide probably interferes with translocation. These two factors may combine to produce necrosis of the older leaves. The deficiency of potassium within the plant may be the result of damage to the root system by the oxidation and deposition of iron and manganic oxides on the root surface and in the root cells. The partial recovery of affected plants, especially under favorable weather conditions, may be attributed to the generation of new roots.

The ameliorative effect of potassium to which numerous investigators (6, 115, 116, 142) have drawn attention may be ascribed to the peculiar ability of potassium to mobilize the deposits of iron in the tissues. This may be attributed to greater citric acid production by an increase in the potassium supply as noted by Cooil with Guayule (53).

Iron toxicity is so often equated to manganese deficiency (221, 238) that it is necessary to emphasize that in none of the descriptions of the disease is there the vaguest hint of a manganese deficiency. Indeed a remarkable feature of the disease is that the unaffected portions of the older leaves and more especially the younger leaves remain green and healthy. If manganese is involved at all in the disease it is more likely that it will augment the toxic effect of iron rather than counteract it. Johnson's (124) observation of brown spots on the older leaves of rice plants grown in solutions high in manganese and Kelly's (134) report on the dieback of tips and browning of leaves of cereal crops grown on certain manganiferous soils of Hawaii suggest that excess

manganese also may be a factor in the causation of the physiological disease of rice associated with poor drainage. The iron-manganese ratio of the external solution on which Shive and co-workers lay so much stress has little meaning in the case of rice for two reasons: (i) the conclusions from experiments with iron and manganese at the low concentrations tolerated by upland crops may not be extrapolated to the extraordinarily high concentrations at which these elements are found in highly reduced submerged soil; (ii) the oxidizing environment in the immediate vicinity of rice roots will alter drastically the ratio in which these elements are present in the bulk of the soil solution.

3.7 The Increase in Solubility of Manganese

Studies on manganese in relation to rice are few in number and difficult to interpret but they suggest that the increase in solubility of manganese on submergence may, within limits, be beneficial to rice. ✓

Aiyer (5) studied the influence of increasing concentrations of manganese on the growth of rice in culture solutions. He noted that below one p.p.m. of manganese deficiency symptoms appeared. These are described as a stunting of growth, chlorosis of the leaves and a constriction and failure of the shoot to unroll. Growth increased up to 20 p.p.m. which was found to be the optimum level. 50 p.p.m. caused chlorosis which became more severe at 100 p.p.m. Aiyer concluded that rice ✓ required manganese, along with iron, in much larger quantities than other minor elements.

Kapp (128) reported the deleterious effects of high concentrations of manganese on rice in culture solution studies. According to Kapp at manganese concentrations of 1-5 p.p.m. the plants were dark green. As the manganese concentration was increased they became chlorotic and the roots became "spindly" and at 50 p.p.m. there was a severe reduction in yield.

Johnson's (124) studies are interesting because they suggest that, at least in culture solutions, the Fe:Mn ratio may be more important than the absolute concentrations of the elements. But the wide variation in the nature and reaction of the culture solutions and the sources of iron and manganese coupled with the somewhat inconsistent results he obtained makes it extremely difficult to judge the most favorable Fe:Mn ratio. Despite these limitations and the probability that much of the iron may not have been in true solution the results indicate that with increase in concentration of manganese chlorosis and retardation of growth became more severe. In mild cases the chlorosis was cured by the application of ferrous sulfate to the foliage.

Tokuoka and Gyo (236) made the unusual study of the effect of manganese in concentrations varying from 1- 1000 p.p.m. in a culture solution added to rice grown in soil in pots. It is not clear what inference these workers drew from their observation that the best yield was obtained with 5 p.p.m. manganese in the culture solution.

The results of field observations appear to be more enlightening. They indicate that rice may suffer from manganese toxicity and even manganese deficiency under field conditions.

Kelly (134) found that when rice was grown as a lowland crop on certain manganiferous soils of Hawaii the plants turned yellow and made no growth. He attributed this to manganese toxicity. Koenigs (138) noted that a decline in rice yields occurred when the layer of iron and manganic oxides formed below the plow sole of paddy fields was plowed into the top soil. Aiyer (5) suggested that excess of manganese may render the Fe:Mn ratio unfavorable to rice.

From Japan come reports of manganese deficiency and response to the application of the element. Seventeen percent of the total rice acreage in Japan is estimated to be deficient in manganese. Deficiency is confined to sandy soils which have been long under cultivation and have had their manganese reduced, leached, and deposited at lower levels. In field trials good responses have been obtained and manganous sulfate at the rate of 1-10 kg per hectare is recommended for these soils. Sprays at the rate of 1-10 kg per hectare are also used.

3.8 The Presence of Sulfides

The presence of sulfides in submerged soils raises the problem of H_2S toxicity.

Hydrogen sulfide being an inhibitor of the iron-containing enzymes cytochrome oxidase, catalase, and peroxidase, is toxic to plants. In the case of upland plants H_2S toxicity is perhaps only of academic interest but in lowland rice culture it can be the cause of serious losses and even crop failure on certain soils. Most paddy soils, fortunately, do not build up toxic concentrations of H_2S , for any H_2S formed by the reduction of sulfate and by the anaerobic decomposition of proteins is almost completely removed from solution as the sparingly soluble ferrous sulfide. But in soils low in iron such as the old sandy paddy soils of Japan the so-called degraded paddy soils -- this protective mechanism cannot operate and H_2S accumulates in the soil solution.

No large accumulation of H_2S is necessary for injury to root cells. Doi (70) has shown that H_2S at concentrations as low as 9×10^{-6} molar decreased protoplasmic streaming in root cells of many crop plants while a concentration of 6.3×10^{-4} molar completely inhibited it. Mitsui and co-workers (163) have demonstrated the injurious effects of H_2S on rice plants at even lower concentrations. Exposure of rice roots to a solution containing 0.07 p.p.m. H_2S for 90 hours was sufficient to cause the wilting of 42 percent of the leaves at the end of a further 200 hours. At H_2S concentrations of the order of 2 p.p.m. the same degree of wilting was observed at the end of 48 hours contact of the roots with the solution.

The preliminary studies of Mitsui and his associates indicated that H_2S injury was a function of the concentration of H_2S in the solution and the time of exposure of the plants to it. In further studies they (162) showed that passing H_2S through the culture solution at the rate of two bubbles a second for 30 minutes caused a marked reduction in ion accumulation, water absorption and protein synthesis during the subsequent 23 hours. The decrease in ion accumulation was not uniformly distributed among the various ions: the accumulation of phosphate and potassium was suppressed altogether and that of silica markedly retarded while calcium accumulation was reduced only 3 percent. Baba and co-workers (19) confirmed the inhibition of potassium and silica uptake by H_2S but found no evidence of reduced phosphate absorption. They also found that protein synthesis was retarded and attributed it to the retardation of aerobic respiration, by H_2S .

In the light of these laboratory studies and of the principles underlying sulfate reduction in submerged soils it is interesting to consider the symptoms, etiology, and control of a certain disease of rice called "Akiochi" or autumn disease in Japan.

This disease has been described by Dion (68) as follows: "Growth of the paddy plant is very vigorous in the early stages and it is expected, at first sight, to give a good harvest. In the later stages, however, the plant is very often severely attacked by sesame-spot and sometimes by rice-blast disease. As a result, its leaves die one by one, beginning with the lower ones. The rice plant therefore has a very miserable appearance at harvest time, and the yield of grain is very small." According to Mitsui (161), the roots of the diseased plants are white in color in contrast to the reddish-brown color of healthy roots, and cortex is destroyed. The disease is confined to the degraded paddy soils. Investigations during the past decade have shown that the disease is due to H_2S injury.

The occurrence of this disease on the degraded paddy soils is understandable because the protective action of iron, to which reference has already been made, is absent. The sudden appearance of the symptoms in late summer is not surprising because production of H_2S can take place only after the soil has undergone considerable reduction; also this is the time when the oxygen supply to the roots is reduced (7, 208). The susceptibility of rice on these soils to fungal infections follows from the decrease in the absorption of chiefly potassium and silica by the retardation of aerobic respiration of the root cells by H_2S .

The common remedial measures are: (i) avoiding the use of ammonium sulfate; (ii) application of materials containing iron, such as lake and river muds and red upland soil; (iii) controlling the pH between 5-5.5 (131); and (iv) aeration of the soils by draining the fields (176).

3.9 Increase in Availability of Silica

Silicon is not generally recognized as an essential element and direct beneficial effects of silica on upland crop plants are discounted (204). But in the case of the rice plant there is evidence that increased absorption of silica is beneficial.

Minabe (159) found that the addition of silicic acid to rice grown under upland conditions caused the development of a vigorous root system and an increase in the dry weight of roots. But this may be due to increased availability of phosphate (204). Ishibashi (110), however, claimed that, in water culture experiments, addition of silicic acid caused an increase in growth and in yield of straw and grain, the effect being most marked at high levels of nitrogen. In the absence of silica brown spots were observed on leaves, especially in the high nitrogen treatments. Okawa and Tanaka (174) reported that silicic acid counteracted the harmful effects of excess nitrogen and that growth and yield were increased by silicic acid.

The role of silica in increasing resistance of the rice plant to fungal infections seems to be better substantiated.

Yoshii (255) found that resistance to blast and the percentage of silica in the leaf blade of rice plants were proportional to the amount of SiO_2 in the culture solution. Ishizuka and Hayakawa (111) found that silica deficient plants were seriously affected when sprayed with the spores of Piricularia Oryzae Gay, and that a deficiency of magnesium aggravated the disease. Suzuki (231) noted that infection by Piricularia Oryzae was less on rice grown on flooded soil than on well drained soil and ascribed it to the greater silication of the epidermal cells. The number of silicated epidermal cells per unit area of leaf, the thickness of the silicated outer walls of the epidermal cells and also the number of silicated stomates were higher in the flooded than in the well drained treatment.

The greater availability of silica in a submerged than in a well drained soil was in an earlier section attributed to increase in pH, reduction of ferric-silica complexes and the increase of the amount of silica in solution. There is a possibility that yet another factor may operate in a reduced soil for Lewin (146) has shown that reduced sulfur compounds stimulated the uptake of silica by diatoms.

3.10 The Absence of Nitrates, the Presence of Nitrites, and the Accumulation of Ammonia

The disappearance of nitrates, the formation of nitrites, and the accumulation of ammonia in submerged soils raise two problems of great physiological interest: first, the relative merits of nitrate and ammonium as the source of nitrogen for rice; and secondly, the question of nitrite toxicity.

The relative merits of nitrates and ammonium salts as fertilizers for rice has been the subject of innumerable studies since Kellner (132), in 1882, demonstrated the superiority of ammonium salts to nitrates as fertilizers for lowland rice. The early experiments in Japan have been reviewed by Kelly (133) who also made a systematic study of the assimilation of nitrogen by the rice plant. The results of subsequent investigations have been analyzed by Bartholemew (20) and more recently by Anderson and associates (13). Additional information is available in a recent FAO publication (109). It is unnecessary, therefore, to consider this topic in detail again. Suffice it if it is stated that Kellner's finding that ammonium salts are superior to nitrates as fertilizers for lowland rice has been confirmed. It must be noted however in some trials nitrates have been nearly as good as ammonium salts and in a very small number of cases they have proved to be even superior to ammonium salts while in no case have nitrates reduced yields.

Although there is practical unanimity about the superiority of ammonium salts to nitrates as the source of nitrogen for rice there is no such agreement about the reasons for it. Among the many reasons which have been adduced for the inferiority of nitrates are: (i) losses due to leaching and denitrification; (ii) inability of the rice plants to utilize nitrate; and (iii) toxicity due to nitrites. Of these, the first is clearly intelligible but the other two explanations though still widely held are not sustained by the available evidence.

The theory that the rice plant could not utilize nitrate was first advanced by Kelly (133) in 1911 to account for his failure to make rice seedlings grow in culture solutions in which nitrogen was supplied as sodium nitrate. Numerous subsequent workers experienced the same difficulty: the plants in nitrate culture solutions became chlorotic and died though the plants in solutions containing ammonium salts as the source of nitrogen were green and healthy. But Gile and Carero (84) and also Bartholemew (20) showed that rice could be grown in culture solutions with nitrates as the source of nitrogen if the culture solutions were prevented from becoming alkaline. Gericke (86) confirmed these observations and from his exhaustive study of the plant food requirements of rice concluded: "The diverse results obtained in respect to the use of nitrate ammonium salts can be explained by factors that affect iron availability." This conclusion was recently verified by Lin (147) who showed that rice seedlings grew equally well in culture solutions with sodium nitrate as source of nitrogen as in culture solutions with ammonium sulphate provided sodium thioglycollate, a complexing agent for iron, was added to the nitrate solutions to prevent the precipitation of iron. It is therefore a matter of great surprise to find Bonner (28) stating in his recent book on plant biochemistry that "ammonia is utilized in preference to nitrate by rice which is apparently unable to reduce nitrate, at least in the seedling stage."

Although early workers were convinced that nitrates were ineffective as fertilizers for lowland rice in the early stages of growth they suggested that in the later stages of growth nitrates might be

beneficial. Kellner (132) found that nitrate was more effective than ammonium salts as fertilizer for rice in the later stages of growth, in swamp soil cultures and that a combination of the two forms gave the best results. Kelly (133) reported that nitrates seemed to exert a stimulating effect when applied, at the time of heading, to pot cultures of rice. These findings are difficult to interpret because in these experiments any direct beneficial effect that nitrate may have had on the rice plant must have been confounded with the influence on the rice plant of the decrease in reducing intensity of the soil following the addition of nitrate. The findings of Dastur and co-workers purport to support the view that rice has a preference for ammonia in the early stages of growth and for nitrate in the later stages, under conditions precluding interference by soil factors.

Dastur and Malkani (60) studied the absorption of nitrogen by rice seedlings grown in soil or in culture solutions and then transferred to one salt and mixed salt culture solutions. Plants in the early stages absorbed more nitrogen from ammonium sulfate than from potassium or sodium nitrate but older plants absorbed more nitrate than ammonium nitrogen. Absorption of NH_4^+ was greatest from ammonium sulfate among ammonium salts and absorption of nitrate was greatest from ammonium nitrate among the nitrates used. They attributed the difference in absorption of the two forms of nitrogen at the two stages of growth to changes in permeability of the protoplasm of the root cells. In a further study Dastur and Kalyani (59) attempted a physico-chemical explanation. They suggested that the greater absorption of ammonium ions by roots in the early stages of growth was due to the greater affinity of the protoplasm of the root cells for cations because the pH of the protoplasm of young roots was on the alkaline side of the iso-electric point. As the plant grew older the pH of the protoplasm changed and was on the acid side of the iso-electric point. This was believed to favor the absorption of nitrate with its negative charge.

On the basis of these studies Dastur and his associates suggested that a mixture of ammonium sulfate and potassium or sodium nitrate was superior to ammonium sulfate alone, as the source of nitrogen for rice. Dastur and Pirzada (61) claimed to have confirmed this in their pot culture studies but when Dastur attempted to test his hypothesis on a field scale he was disillusioned. In a series of twenty-nine experiments, Dastur (58) found that a mixture of ammonium sulfate and sodium nitrate was superior to ammonium sulfate alone in six, inferior in five, and equal in the remainder. These results do not constitute a refutation of Dastur's hypothesis for it is impossible to evaluate the direct effect of nitrate on the plant in the face of the influence of nitrate on the reducing intensity of a submerged soil. But there are other grounds for rejecting Dastur's hypothesis.

First, his results clearly show that the pH of the sodium nitrate culture solutions had risen considerably -- in some instances to a pH as high as 8.5. The failure of the rice plants to absorb nitrate may thus be laid to iron deficiency -- a phenomenon which was recognized

by Gile and Carero as far back as 1916 and confirmed later by Bartholemew (20), Gericke (86) and Lin (147). Secondly, his theory of the influence of the permeability of the protoplasm to NH_4^+ and NO_3^- ions is not tenable in the light of modern knowledge on the metabolic nature of ion accumulation and the demonstration of the absorption of anions and cations in roughly equivalent amounts.

A hitherto unsuspected aspect of the nitrogen nutrition of rice has, in recent years, received recognition. It is the toxicity of ammonium salts to rice. Lin (147) reported that rice seedlings grown in culture solutions with ammonium sulfate as the source of nitrogen showed tip burn. Bonner (27) found that ammonium salts were toxic to rice seedlings at concentrations over 17.5 millimolar. Doi and co-workers (71) found that at concentrations higher than millimolar ammonium sulfate retarded protoplasmic streaming of root hairs and growth of roots of rice. More recently Malavolta (149) has obtained evidence of the better growth of rice in culture solutions containing nitrate with a trace of molybdenum than in ammonium cultures. He noted an accumulation of ammonia in the plants from the ammonium cultures which was not accompanied by an increase in asparagine or glutamine and attributed this to a defective detoxication mechanism.

Ammonium toxicity is probably no problem in normal paddy soils. But in soils heavily manured with organic manures and in heavily fertilized sandy soils the concentration of NH_4^+ in the soil solution may attain injurious levels.

A common though unfounded objection to the use of nitrates as fertilizers for lowland rice is that nitrites are produced in toxic amounts. The theory of nitrite toxicity from the use of nitrates on lowland rice was propounded by early Japanese workers, affirmed by Kelly in Hawaii and by Harrison and Aiyer in India and accepted uncritically by workers in the Orient for decades. Thanks chiefly to the researches of American workers this view is now losing ground. American investigators showed, as already indicated, that nitrite concentrations in excess of 3 p.p.m. are not encountered in submerged soils fertilized with nitrate; that concentrations of this order have only a transitory existence; and that during the greater part of the growing season nitrites are present only in traces. They also drew attention to experiments in the Philippines (198) which showed that rice could be grown in culture solutions with nitrite as source of nitrogen and to the common use of nitrate as fertilizer for lowland rice in some of the southern states. These observations have been confirmed by plant physiologists and field experimentalists.

According to Bonner (28) though nitrite ions are toxic to plants at high concentrations they are utilized by plants if applied in concentrations less than 50 p.p.m. Duisberg and Buehrer (72) noted that even at a concentration of 26 p.p.m. nitrite nitrogen barley suffered no injury. And Eggleton (74) reported that an application of sodium nitrite at the rate of 3 cwt. per acre to grass caused "no visible signs of distress."

In the light of present knowledge it is interesting to enquire into the origin of this popular fallacy. Two sources frequently cited in support of the theory of nitrite toxicity are the works of Daikuhara and Imaseki (56) and Kelly (133). Daikuhara and Imaseki, noted the accumulation of nitrite in enormous amounts in their laboratory studies of denitrification. Attention has already been drawn to the highly artificial conditions under which they obtained these results. The conditions under which they demonstrated nitrite toxicity are no less extraordinary. They placed rice plants in 0.1 percent potassium nitrite solution and observed their death after five days. Kelly's conclusions, though probably incorrect, are less blameworthy. He noted that rice seedlings in sand cultures with sodium nitrate as source of nitrogen turned chlorotic and died while the ammonium sulphate cultures flourished. He noted that the pots which were worst affected had a nitrite concentration exceeding 5 p.p.m. and inferred that nitrites were the cause of the pronounced injury. An equally plausible explanation is that the higher nitrite concentration in the severely affected pots was due to more extensive decay of roots and the consequent increase in reduction of nitrate in these pots than in the less severely affected pots. The association of severe injury to plants with a nitrite concentration of 5 p.p.m. drove Kelly to the conclusion that nitrates would be toxic to rice "if nitrites accumulate to any considerable extent." Unfortunately, in a later publication (135), but without fresh evidence, he left a strong impression that the use of nitrates on rice would lead to nitrite toxicity.

The evidence is clear that the inferiority of nitrates to ammonium salts generally as fertilizers for rice not due to the inability of rice to assimilate nitrate nor to nitrite toxicity, but to loss of nitrate by leaching and denitrification.

Denitrification is normally to be deplored because it represents the loss of a valuable plant nutrient. But in acid soils with a tendency to accumulate reduced iron and manganese in concentrations that may be injurious to rice it is questionable whether denitrification is a thing to be regretted. Reference has already been made to the stabilizing effect of nitrate on the redox potential and the retardation of the reduction process in the soil by nitrate functioning as hydrogen acceptor to the products of anaerobic metabolism. Does this not suggest a novel and valuable role for nitrates in rice production on certain very poorly drained soils where diseases probably associated with accumulation of reduced products are a problem? It is left to future research to determine the efficacy and the economics of the use of nitrates, especially potassium nitrate, as a remedy for the physiological disease of rice called "mentek" in Java, "penyakit merah" in Malaya and "browning disease" in Ceylon.

3.11 The Anaerobic Decomposition of Organic Matter

The anaerobic decomposition of organic matter may affect the rice plant through (i) the products of decomposition; and (ii) its influence on chemical equilibria in the soil.

Of the products of decomposition, ammonia is the most important. Its value as a plant nutrient needs no emphasis for nitrogen holds the key to productivity in rice as it does with the other cereal crops. But some advantages of organic manures as a source of nitrogen to the rice plant call for comment.

The chief advantages of the use of an organic source of nitrogen are: (i) leaching losses are minimized; and (ii) ammonium toxicity is averted. In the early stages of submergence, a high proportion of the ammonium added as fertilizer is held as an exchangeable cation by the soil colloids. As reduction proceeds, however, there is increasing competition for the exchange sites, by Fe^{+2} and Mn^{+2} ions. Consequently an appreciable amount of ammonium will be displaced into the soil solution and be lost in the drainage. With organic manures the situation is different: ammonia is released gradually and the period of maximum ammonia production coincides with the period of maximum demand by the crop. Thus any considerable accumulation of ammonium in the soil solution, with its attendant disadvantages, is averted. In this connection it is interesting to note that Bonner (27) observed a marked beneficial effect of manure on rice grown in sand cultures with standard culture solutions. This effect could not be duplicated by alteration of the composition of the nutrient solution within wide limits. The influence of the manure was shown to be quantitatively attributable to the organic nitrogen content of the manure. The conclusion was that the nitrogen of the organic matter served as a supplement to the low concentration of free ammonium salts which are tolerated by plants.

Of the organic acids produced during the anaerobic decomposition of organic matter, butyric acid is perhaps the most important. It is present in appreciable amounts in the early stages of the decomposition, may persist in acid soils, and is toxic to plants. Mitsui and co-workers (162) have shown that butyric acid at less than 0.1 mol per liter can cause a marked decrease in nutrient uptake. The common failure of rice seedlings on newly manured fields may be attributed to the toxic effects of butyric acid and carbon dioxide.

Among the gaseous products, methane merits special attention. Apart from the beneficial effect of methane on the algal film to which Harrison and Aiyer had drawn attention there is evidence that methane may have a direct beneficial effect on the rice plant itself. Vlamis and Davis (243) found that, while bubbling nitrogen through culture solutions had no effect on the growth of rice and decreased that of barley and tomato, passing methane inhibited growth of the tomato plants completely, reduced the growth of barley more than nitrogen did but increased the root growth of rice 70 percent over the control.

This observation taken in conjunction with Borasio's (30) claim to have demonstrated experimentally that a substantial portion of the carbon assimilated by the rice plant comes via the roots suggests that methane, carbon dioxide and perhaps also the organic acids

may be playing hitherto unsuspected roles in the nutrition of the rice plant.

The influence of the biochemical activity associated with the anaerobic decomposition of organic matter on chemical and physico-chemical equilibria in submerged soils was discussed in an earlier section. All that need to be said now is that the addition of organic matter to a submerged soil will accelerate the reduction process and help to keep in solution a high proportion of the reduced iron and manganese, in the form of complexes.

In the light of this short review of the influence of the anaerobic decomposition of organic matter in paddy soils on the rice plant it is interesting to consider the merits and demerits of the age-old practice of applying organic manures to rice soils.

Organic manures are generally effective in increasing yields, although ill effects of the practice have been observed on certain poorly drained soils (89, 241). The benefits of manuring have been attributed to (i) the plant nutrients; (ii) improvement in soil structure (89, 109, 227); and (iii) improved aeration of the rice roots. Of these reasons only the first can stand scrutiny.

The idea of the improvement of soil structure is the result of the uncritical application of upland experience to submerged soils. To make confusion worse confounded this idea is often coupled with the mistaken notion that decomposition and loss of organic matter is more rapid in flooded than in upland soils (227).

It is not clear what function these writers have assigned to soil structure in the production of a crop which does not require aeration of the root environment and which grows under conditions where mechanical obstructions to root growth are practically non-existent.

The theory of improved aeration of the rice roots by the application of bulky organic manures has already been refuted and requires no further comment.

The benefits of organic manuring thus reside in the gradual release of plant nutrients, especially nitrogen.

What are the drawbacks of the use of bulky organic manures on paddy soils? They are briefly: (i) acceleration of denitrification; (ii) probable injury to rice plants from carbon dioxide and butyric acid; (iii) the production of large amounts of soluble iron and manganese.

It would appear that the practice of green manuring may be discontinued with advantage, where fertilizers are available cheaply.

4. THE MAIN EXPERIMENT

4.1 Plan of the Experiment

The survey of the literature revealed that the better growth of rice on submerged than on well drained soil is associated with the increase in the concentration of certain elements, especially iron. It also indicated that high concentrations of reduced products could be injurious to rice. It was surmised, therefore, that if rice were grown over a sufficiently wide range of reducing intensities it would be possible to delimit the range over which the plant would not be adversely affected by a deficiency of these elements on the one hand and excess of reduced products on the other. It was believed that this range might be characterized with some success chemically and physico-chemically.

In the chemical characterization the emphasis was on those constituents whose concentrations are most liable to vary with the intensity of reduction, namely, NO_3^- , NO_2^- , NH_4^+ , Fe^{+2} , Mn^{+2} , and total oxidizable matter. The concentration of these constituents in the soil solution and of Fe^{+2} and Mn^{+2} in the soil were determined at intervals during the period of growth.

The physico-chemical properties studied were pH and redox potential of the soil, and the specific conductance of the soil solution.

It was believed that a range of reducing intensities could be obtained by varying the pH, the organic matter content, and the drainage conditions of the soil. To this end, these factors were studied at three levels in a $3 \times 3 \times 3$ factorial experiment laid down in the form of a 9×9 quasialatin square in which the second order interaction was partially confounded with the rows and the columns. The design of the experiment is given in Table 19 of the Appendix.

It was felt that this design would provide a wide range of reducing intensities and at the same time enable the segregation of the effects of pH, organic matter, and drainage on yield, individually, and the interaction effects at the first order level and also the estimation of the pH x organic matter x drainage interaction with some sacrifice of accuracy. The chemical and physico-chemical data, it was felt, could be used to interpret the observed effects.

4.2 Materials and Methods

4.21 Materials

The Mardin silt loam used for the experiment had the following analysis* by the methods of Peech and English (185).

* This analysis was furnished by the Soil Testing Laboratory at the instance of Prof. Peech.

pH	%	lbs. per 2,000,000 lbs. of soil					
		P	Ca	Mg	K	Fe	Al
4.85	3.05	1	450	50	160	20	300

The three pH levels were 4.85, 5.7, and 6.0. The two higher pH levels were obtained by treating the Mardin silt loam with finely ground limestone at the rate of 3 and 4 tons per 2,000,000 lbs., respectively. The limed soils stood in a moist state for four weeks in the greenhouse before use and had an unusually high electrolyte content at the start of the experiment.

The three levels of added organic matter were 0.0 percent, 0.2 percent and 0.4 percent ground oat straw.

The three levels of drainage were (i) moist, well drained; (ii) submerged, with drainage at a rate corresponding to 0.4" per day; and (iii) submerged, no drainage.

4.22 Greenhouse Procedure

The Mardin silt loam treated appropriately with respect to pH and organic matter levels and fortified with a basal dressing of 2,000 lbs. per acre* of a 5-10-5 fertilizer mixture consisting of ammonium sulfate, triple superphosphate and potassium chloride was placed in 81 three gallon, glazed earthenware pots, 20 lbs. to the pot. Provision was made for drainage from the bottom of the pots.

The variety of rice used was Zenith.** The seedlings were raised in a submerged sand culture containing Hoagland solution fortified with 10 p.p.m. Fe as sodium ferric ethylenediamine tetracetate. The plants were eight weeks old when they were topped at a height of 18" and transplanted in the moist soil one plant per hole to give 6 plants per pot. The drainage treatments were then begun.

The well drained pots received sufficient distilled water to bring the soils just to field capacity. Every effort was made to keep the moisture content at this level, during the experiment, without causing undue loss of nutrients by leaching. The pots of the submerged treatments were filled to the brim and the 2" of standing water in these pots was maintained by the daily addition of distilled water. The drainage treatment for the submerged soils with drainage consisted of the removal of half a liter of water daily from the bottom of the pots. This corresponded to a loss of 0.4" daily by drainage and the renewal of the soil solution approximately once in eight days.

The soil solutions used for analyses were the percolates collected from the bottom of the submerged pots and the displaced soil solution from the well drained pots. They were collected in the strict absence of air in 250 ml. Erlenmeyer flasks which had previously been

* Per 2,000,000 lbs. of soil.

** Seed obtained through the courtesy of Dr. Roy C. Adair of the U.S.D.A.

filled with nitrogen. The flasks were then stored in a refrigerator till analysis.

The soil samples were obtained by pushing a glass tube 15 mm. in internal diameter down to the bottom of the pots, stoppering it and withdrawing it with a circular motion. The air was flushed out with nitrogen, the ends of the tubes, stoppered and the samples stored in a freezer till analysis.

4.23 Analytical Procedures

4.231 Physico-chemical

Redox potentials were determined in situ. Two blank platinum electrodes were seated permanently in each pot at a depth of six inches from the surface of the soil. They were placed near the center of the pot and stood 3" apart on a diameter. The potentials were measured with a Leeds and Northrup vacuum tube potentiometer using a saturated calomel electrode as reference electrode.

pH measurements were made with a glass electrode on subsamples of the soil cores taken for chemical analysis. A 1:1 suspension of moist soil in oxygen-free water was used.

Specific conductance was determined on the percolates at 25°C, with a Conductivity Bridge embodying a cathode ray tube as null indicator, using an immersion cell with a constant of 0.274 reciprocal centimeter.

4.232 Chemical

(a) Percolates

The percolates from the pots were clear and required no filtration. But, for the analysis of NH_4^+ , NO_3^- , and NO_2^- , interfering substances had to be removed. This was done by a modification of the method proposed by the American Public Health Association for the clarification of water and sewage (12).

Fifty milliliters of the percolate was treated in a 25 x 200 mm. test tube with 5 drops of 10 percent zinc sulfate and a few drops of 25 percent sodium hydroxide to give a pH of approximately 10. The tubes were inverted a number of times and allowed to stand. Precipitates, which were initially white to dark green in color and later turned brown, settled at the bottom. The supernatant liquid* was clear and colorless in the early stages of the experiment. It was pipetted out and used for the determination of NH_4^+ , NO_3^- and NO_2^- . In the later stages the supernatant liquid was pipetted out, mixed with an equal volume of 10 percent sodium acetate at pH 4.8 and decolorized with Darco activated carbon. Sodium acetate was used to minimize the retention of NH_4^+ , NO_3^- and NO_2^- by the activated carbon.**

* Will be referred to as clarified percolate, hereafter.

** Prof. Peech, personal communication.

The analytical procedures for NH_4^+ , NO_3^- and NO_2^- are outlined below.

Ammonium was determined by a modification of the method proposed by Peech *et alia* (186) for the estimation of adsorbed ammonia in cation exchange capacity determinations.

Five milliliters of the clarified percolate was transferred into a 50 ml. volumetric flask containing about 40 ml. of water. Two and a half milliliters of Nessler's solution, prepared according to the directions of Peech *et alia* (186) were added and the mixture made up to mark. The contents of the flask were mixed well, allowed to stand 25 minutes, and the transmittancy read at 410 $m\mu$. on a Coleman Junior Spectrophotometer,* using a 15 mm. cell. Zero to 100 micrograms N as NH_4Cl were used for the standard curve.

In the later stages of the experiment, when the solutions were decolorized with activated carbon in the presence of sodium acetate, 1 ml. of 10 percent sodium tartrate and 2.5 ml. of 10 percent gum acacia were added prior to nesslerization, as recommended by Peech *et alia* (186).

Nitrate. Nitrate was estimated, without interference from nitrite, by the brucine procedure prescribed by Knoll (140). Above 8 p.p.m. nitrate N the standard curve showed a marked tendency to flatten out. In the early stages, considerable dilution of some of the samples was, therefore necessary.

Five milliliters of the clarified percolate were pipetted into a 50 ml. beaker and treated with 0.2 ml. of 5 percent brucine in chloroform. Ten milliliters of concentrated H_2SO_4 was added and the contents of the beaker mixed by swirling. After 5 minutes standing, 10 ml. of water was added, the beaker swirled and the transmittancy was measured after an hour, at 470 $m\mu$. in a 15 mm. cell. Zero to 50 micrograms N as KNO_3 were used for the standard curve.

Nitrite. Nitrite was determined by the method based on the coupling of diazotized sulfanilic acid with α -naphthylamine, as described by Rider and Mellon (201).

A measured volume of the clarified percolate containing less than 5 micrograms nitrite N (considerable dilution was necessary with some samples) was evaporated to dryness, on a steam plate, in a 50 ml. beaker, to drive off the ammonia. The residue was taken up in water and transferred to a 50 ml. volumetric flask. One milliliter of sulfanilic acid solution (prepared by dissolving 0.60 gm. of sulfanilic acid in 70 ml. hot water and 20 ml. conc. HCl and bringing up to 100 ml.) was added. The contents of the flask were mixed and allowed to stand for 5 minutes. Then 1.0 ml. of α -naphthylamine solution (0.60 gm. of the reagent and 1.0 ml. conc. HCl diluted to 100 ml. with water) was added. The pH was adjusted to 2.0 - 2.5 with filtered 2 molar sodium acetate. The mixture was brought up to volume and the transmittancy read at 520 $m\mu$ in a 15

* Unless otherwise stated all transmittances are on this instrument.

mm. cell. Zero to 5 micrograms nitrite N as NaNO_2 was used for the standard curve.

Oxidizable matter was determined by a modification of the method prescribed by the American Public Health Association (12) for the estimation of the oxygen consuming capacity of sewage.

Oxidizable matter includes soluble Fe^{+2} , NO_2' and S'' among the inorganic constituents, and soluble organic matter that is oxidized under relatively mild conditions. It was believed that this determination would give a measure of the reducing capacity of the soil solution. It is clear that this is an arbitrary determination and has only comparative value.

The method is based on the oxidation of the sample with potassium permanganate under standard conditions. The modified procedure used in this investigation is described below.

Oxidizable matter was the very first determination to be carried out and was run directly on the percolates without any pretreatment.

The sample (the volume used varied from 0.5 ml. to 25 ml.) was added to a mixture of 10 ml. of 0.01 N KMnO_4 and 10 ml. of 1:3 H_2SO_4 , with sufficient water to make a total volume of 100 ml., in a 250 ml. Erlenmeyer flask. The flask was heated in a boiling water bath for 30 minutes along with a blank. By this procedure the factors, (strength of KMnO_4 , acidity of the medium and time of digestion), on which the figure for oxidizable matter depends, were kept nearly constant. Immediately after the digestion 10 ml. of 0.01 N $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution was added and the excess oxalate back titrated against 0.01 N KMnO_4 . The difference between this reading and the blank reduced to a fixed volume of sample was taken as an index of the concentration of oxidizable matter or the reducing capacity of the percolates.

Iron and manganese determinations were run on the percolates which had been preserved from oxidation and precipitation by the addition of 1 ml. of conc. H_2SO_4 to the 175-200 ml. of percolates left in the collection flasks after the other determinations.

Iron. Iron was estimated, after reduction with hydroxylamine, by the o-phenanthroline method as described by Fortune and Mellon (78).

The sample, varying in size from 0.1 ml. for the percolates from the highly reduced soils to 25 ml. for the well drained soils, was pipetted into a 100 ml. volumetric flask. One milliliter of 10 percent hydroxylamine hydrochloride solution was added and the contents diluted to about 75 ml. with water. Five milliliters (10 ml. for samples high in Fe) of an 0.1 percent solution of o-phenanthroline monohydrate in water was added. The pH was adjusted to about 7 with 6 N NH_4OH , the contents made up to volume and mixed. The transmittancy was determined at 508m μ . A 22 mm. cell and 0-50 micrograms Fe as ferrous ammonium sulfate in acid solution for the standard curve were used for the percolates

from the well drained soils while a 10 mm. cell and a range of 0-200 micrograms Fe were used for the percolates from the submerged pots.

Manganese. Manganese was determined by the periodate method according to the procedure prescribed by Peech *et alia* (1936), after the oxidation of organic matter and removal of chlorides by evaporation with nitric acid.

Five to twenty-five milliliters of the percolate (according to its manganese content) was pipetted into a 50 ml. beaker and evaporated to dryness on a steam plate. Ten milliliters of conc. HNO_3 was added and the evaporation repeated. The residue was treated with 35 ml. of water and 5 ml. of 85 percent H_3PO_4 . To the clear, colorless solution obtained, 0.3 gram of sodium periodate was added and the contents of the beaker brought to boiling on a hot plate. After cooling the solution was transferred to a 50 ml. volumetric flask and made up to volume with 5 percent phosphoric acid solution. The solution was mixed well and the transmittancy determined at 530 m μ using a 22 mm. cell for the percolates from the well drained soils and a 15 mm. cell for the rest. Zero to 50 micrograms Mn were used for the standard curves.

(b) Soil analyses

The following series of determinations were carried out on soil samples: (i) pH, moisture content; (ii) oxidizable matter, and Fe^{+2} , in 0.1 N H_2SO_4 extracts; (iii) total Fe and Mn, and also P in Morgan* extracts.

The soil samples which had been preserved in the sampling tubes in the freezer were extracted from the tubes after thawing. Samples of the well drained soils had to be dug out of the tubes while the others were eased out in the form of coherent cylindrical masses.

The amount of soil in the tubes varied from 10 to 15 gm. in the moist state. About half the sample was used for the Morgan extraction and the remainder used in roughly equal amounts for (i) the pH and moisture determinations, and (ii) for the sulfuric acid extraction.

pH and moisture determinations were run on the same sub-sample. The sample was transferred to a tared 30 ml. beaker and the weight of moist soil quickly determined. An equal weight (volume) of oxygen-free distilled water was added, the beaker swirled and the pH determined with a glass electrode. The soil adhering to the electrodes was washed into the beaker with a jet of water. After the expulsion of the bulk of the water on a steam-plate the soil was dried further in an oven at 105°C for 24 hours.

The sample for the sulfuric acid extraction was transferred into a 50 ml. Erlenmeyer flask which had previously been weighed with 25 ml. of 0.1 N H_2SO_4 and a rubber stopper. The air was immediately flushed out with nitrogen, the flask stoppered and weighed again. The flask was gently swirled and allowed to stand with occasionally swirling for 24

* A solution of 100 gm. $\text{NaC}_2\text{H}_3\text{O}_2 \cdot 3\text{H}_2\text{O}$ with 30 ml. of 99.5 percent acetic acid made up to liter with water will be referred to as Morgan's solu-

hours. One milliliter of the clear supernatant liquid was pipetted off and the oxidizable matter determined by the procedure outlined earlier. A sample, varying from 0.1 - 1.0 ml. according to the nature of the soil, was likewise pipetted off and used for the determination of iron by the o-phenanthroline method with one modification -- the reduction with hydroxylamine was omitted.

The procedure was modified slightly for the preparation of the Morgan extracts in an attempt to keep the soil:extractant ratio as close as possible to 1:5. The sample was transferred to a 50 ml. Erlenmeyer flask which had previously been flushed out with nitrogen and tared with its rubber stopper. Once the weight of the moist soil was ascertained a rough allowance was made for the moisture content, on the basis of preliminary experience, and Morgan's solution added from a burette to give a soil:extractant ratio of approximately 1:5.

The flasks were allowed to stand for 24 hours with occasional swirling and the solution filtered through fluted filter paper. The clear, light brown solution, which gradually acquired a deeper color, was used for the determination of iron, manganese and also phosphate (with one set of samples).

Iron and manganese were determined by the procedures used for the percolates.

Phosphate. Phosphate was analyzed by a modification of the benzene-isobutanol method described by Martin and Doty (153).

Five ml. of the clear Morgan extract was transferred to a 25 x 200 mm. test tube and 15 ml. of a 1:1 mixture of thiophene - free benzene and iso-butanol added. Five milliliters of ammonium molybdate solution (50 grams ammonium molybdate in 400 ml. of 10 N sulfuric acid diluted to 1 liter) was added and the mixture shaken for 15 seconds. Ten milliliters of the organic layer containing the phosphomolybdic acid in solution was transferred into a 50 ml. Erlenmeyer flask with the aid of a pipette fitted with a suction device and 10 ml. of ethanol, with two percent concentrated sulfuric acid in it, added from the same pipette. The reduction of the heteropoly acid was effected with 1 ml. of dilute stannous chloride solution. (One milliliter of a solution of 10 gm. $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 25 ml. conc. HCl diluted 200 times with 1N H_2SO_4 .) The blue color developed was measured after one hour, spectrophotometrically at a wave length of 670 $\text{m}\mu$, using a 22 mm. cell. Standards were run with 0-1 microgram P, as KH_2PO_4 , in Morgan solution.

4.3 Results and Discussion

The results of the physico-chemical and chemical analysis of the soil and percolates from each of the eighty-one pots on each of the several sampling dates are given in Tables 1-8 of the Appendix. Tables 9-16 give the mean values of the physico-chemical and chemical determinations

for each treatment. Growth and yield data for the rice plants are detailed in Table 17 of the Appendix and the mean values for each treatment presented in Table 18.

4.31 Physico-chemical Analyses

4.311 pH

The mean pH values of the soils for each treatment on four sampling dates are given in Table 1.

The first point that calls for comment is the discrepancy between the pH value assigned to a soil as "treatment pH" and the observed pH value at the start of the experiment. The three "treatment pH" values 4.9, 5.7, and 6.0 denote the pH values of the Mardin silt loam four weeks after the addition of 0, 3, and 4 tons per acre respectively of ground limestone. The lower pH values observed at the start of the experiment, namely, 4.6, 5.4, and 5.7, reflect the depressing effect of the 2,000 lbs. per acre of 5-10-5 used as basal fertilizer dressing. The effect of the fertilizer mixture on the pH of the soils at the three pH levels is brought out more precisely by the following figures:

Initial pH	pH after fertilization
4.85	4.58
5.68	5.40
5.95	5.72

It may also be mentioned that the pH values observed after liming were appreciably below the expected values -- a matter which was a source of some uneasiness at the time. Conductance measurements, however, revealed an extraordinarily high content of electrolyte in the two limed soils.

The influence of salts on the pH of soils is widely recognized, so much so that pH measurements of soils often are made in normal potassium chloride solution with a view to masking the effect of fluctuating electrolyte content of soils, on the pH (182). Also Piper (*) has suggested that the changes in pH with the soil:water ratio may partly be due to the neutral salt effect while Puri and Asghar (189) have attempted to describe this effect quantitatively by the equation

$$\text{pH} = \text{pH}_0 - K \log c$$

where pH_0 is the pH without salt, c is the concentration of salt in m.l. per 100 gm. of soil, and K is a constant characteristic of the cation.

* Piper, C. S. Soil and Plant Analysis, (Univ. of Adelaide) 1942, p. 9.

TABLE 1
CHANGES IN pH OF SOILS DURING THE PERIOD OF GROWTH

Treatment No.	pH	Treatments		pH on Days from Start			
		Oat Straw %	Drainage	0	18	37	70
I	4.9	0.0	w.d.*	4.6	4.83	5.12	4.9
II	"	"	s.w.d.	4.6	5.66	6.32	6.41
III	"	"	s.n.d.	4.6	5.42	6.36	6.53
IV	4.9	0.2	w.d.	4.6	4.90	5.27	5.2
V	"	"	s.w.d.	4.6	5.68	6.48	6.57
VI	"	"	s.n.d.	4.6	5.64	6.24	6.61
VII	4.9	0.4	w.d.	4.6	4.93	5.21	5.3
VIII	"	"	s.w.d.	4.6	5.60	6.45	6.65
IX	"	"	s.n.d.	4.6	5.50	6.31	6.55
X	5.7	0.0	w.d.	5.4	5.88	6.31	6.3
XI	"	"	s.w.d.	5.4	6.29	6.68	6.95
XII	"	"	s.n.d.	5.4	6.04	6.67	6.99
XIII	5.7	0.2	w.d.	5.4	5.95	6.35	6.3
XIV	"	"	s.w.d.	5.4	6.30	6.73	6.79
XV	"	"	s.n.d.	5.4	6.34	6.67	7.14
XVI	5.7	0.4	w.d.	5.4	6.07	6.41	6.4
XVII	"	"	s.w.d.	5.4	6.39	6.71	6.67
XVIII	"	"	s.n.d.	5.4	6.27	6.64	7.09
XIX	6.0	0.0	w.d.	5.7	6.28	6.40	6.5
XX	"	"	s.w.d.	5.7	6.51	6.92	6.93
XXI	"	"	s.n.d.	5.7	6.45	6.93	6.97
XXII	6.0	0.2	w.d.	5.7	6.30	6.37	6.6
XXIII	"	"	s.w.d.	5.7	6.44	6.75	6.93
XXIV	"	"	s.n.d.	5.7	6.49	6.73	7.09
XXV	6.0	0.4	w.d.	5.7	6.41	6.52	6.6
XXVI	"	"	s.w.d.	5.7	6.64	6.81	6.97
XXVII	"	"	s.n.d.	5.7	6.44	6.71	7.20

* w.d. = well drained; s.w.d. = submerged with drainage; and s.n.d. = submerged, no drainage.

The pH values of all the soils, regardless of organic matter and drainage treatments, have increased with time. The increases are more pronounced in the submerged soils than in the well drained soils. There is a tendency for pH to increase with organic matter content for a given drainage and pH treatment. But this is neither consistent nor appreciable. The pH changes for the 0.0 percent oat straw organic matter treatment may therefore be taken as typical of the pH changes during the season. They are represented graphically in Fig. 1.

The graphs show that the pH values of all soils increase sharply during the first 34 days and then tend towards stability. The pH value of the well drained soil (treatment pH 4.9) tends to be stabilized around 4.9 while the corresponding values for the two higher pH treatments are approximately 6.3 and 6.5 respectively. The relatively sharp increase in pH of the well drained soils during the first 34 days may be attributed to the decrease in electrolyte concentration caused by leaching losses and assimilation. It is worthy of note that the sharp increase in pH is paralleled by a decrease in specific conductance of the percolates from these treatments.

The increases in pH values of the submerged soils at all three pH levels are much more pronounced than those of the corresponding well drained soils and are, no doubt, associated with the reduction of iron and manganese. The pH values of the submerged soils with drainage are higher than those of the submerged soils without drainage, during the initial stages. A glance at rows II and III, XI and XII, and also XX and XI of Tables 10 and 11 of the Appendix reveals that the higher pH values of the submerged soils with drainage is associated with a higher content of reduced iron and manganese and a lower specific conductance.

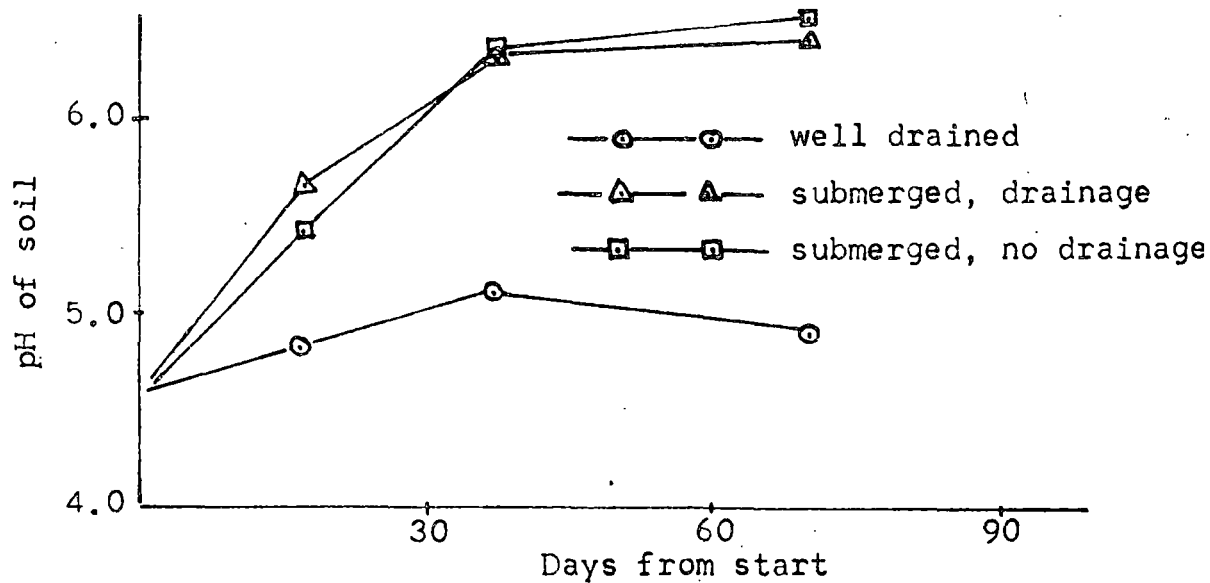
The graphs also indicate that the increase in pH caused by submergence is greatest for the lowest pH treatment and apparently least for the highest pH treatment. If the pH values at which the well drained soils get fairly stabilized are taken as the true pH values of these soils (i.e., the pH values in the absence of excessive amounts of electrolyte) then the pH increases caused by submergence may be represented by the following approximate figures.

Initial pH	Δ pH
4.9	1.5
5.7	0.7
6.0	0.5

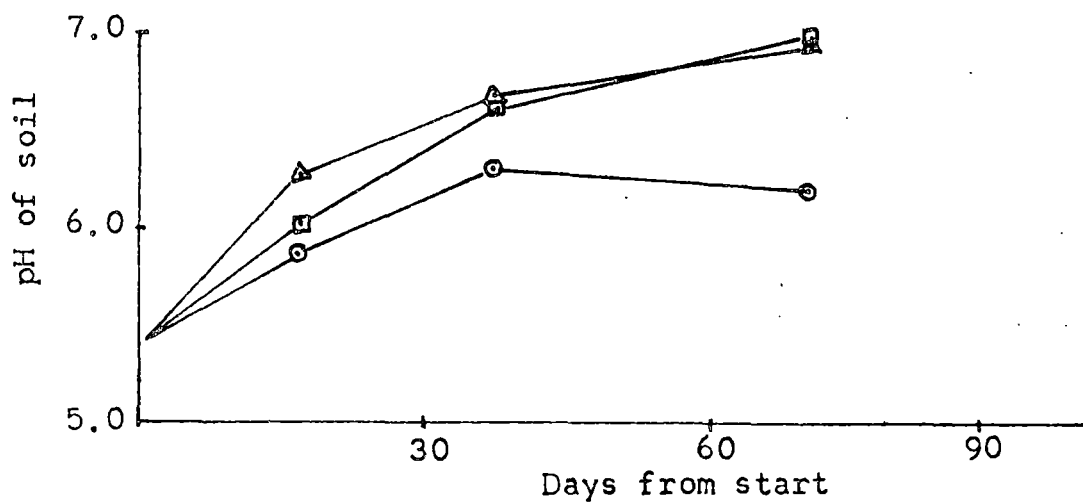
4.312 Specific Conductance

The mean specific conductances, of the percolates taken at intervals during the growing season, for each treatment, are presented in Table 2.

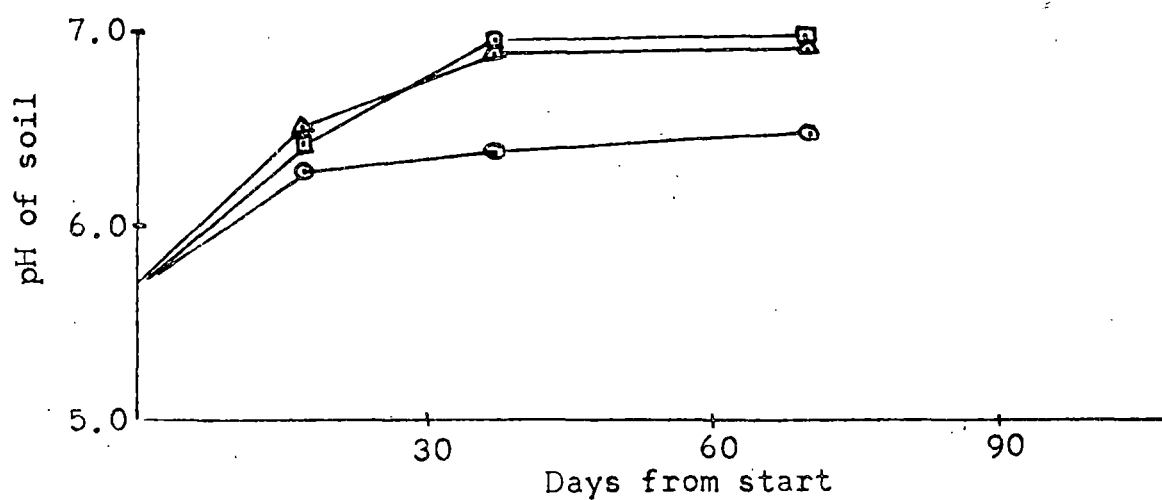
The relatively high specific conductances at the first sampling reflect the fertilizer and lime treatments. Of the three pH



(a) pH 4.9



(b) pH 5.7



(c) pH 6.0

Fig. 1. Changes in pH during period of growth.

TABLE 2

CHANGES IN SPECIFIC CONDUCTANCE DURING THE PERIOD OF GROWTH

Treatment No.	Treatments			Sp. Cond. of Percolates, in Micro Mhos. on days from Start				
	pH	Oat Straw %	Drainage	1	17	34	67	108
I	4.9	0.0	w.d.*	1640	229	95	26	-
II	"	"	s.w.d.	1840	491	469	556	396
III	"	"	s.n.d.	1530	1650	1030	1530	1920
IV	4.9	0.2	w.d.	-	222	48	86	-
V	"	"	s.w.d.	1810	350	560	496	310
VI	"	"	s.n.d.	2040	1290	1120	1570	1830
VII	4.9	0.4	w.d.	2560	266	31	35	-
VIII	"	"	s.w.d.	2070	642	613	547	348
IX	"	"	s.n.d.	2450	2170	1560	2000	1230
X	5.7	0.0	w.d.	3270	534	659	538	-
XI	"	"	s.w.d.	3220	934	958	720	447
XII	"	"	s.n.d.	3840	4600	3270	2370	2610
XIII	5.7	0.2	w.d.	3770	454	403	138	-
XIV	"	"	s.w.d.	3180	1280	833	717	385
XV	"	"	s.n.d.	3390	3810	2220	2050	2050
XVI	5.7	0.4	w.d.	3440	358	196	170	-
XVII	"	"	s.w.d.	3280	1420	846	579	361
XVIII	"	"	s.n.d.	3890	2950	2430	1870	1850
XIX	6.0	0.0	w.d.	4130	829	870	264	-
XX	"	"	s.w.d.	5230	981	964	803	401
XXI	"	"	s.n.d.	4770	3730	2330	2190	2650
XXII	6.0	0.2	w.d.	5010	892	515	137	-
XXIII	"	"	s.w.d.	4980	1310	869	842	515
XXIV	"	"	s.n.d.	4850	2880	2240	2370	1920
XXV	6.0	0.4	w.d.	3570	488	216	247	-
XXVI	"	"	s.w.d.	5330	1390	868	797	358
XXVII	"	"	s.n.d.	6500	3690	1710	2150	1840

* w.d. = well drained; s.w.d. = submerged with drainage; and s.n.d. = submerged, no drainage.

treatments, pH 4.9 has the lowest specific conductance and pH 6.0 the highest. The much higher conductances of the percolates from the limed soils may be attributed chiefly to the nitrates which were present in exceedingly high amounts in these soils.

At the second sampling striking differences are noticeable. The contrast is most marked among the three drainage treatments. The well drained soils register a drastic lowering of conductivity, the submerged soils with drainage a slightly lower reduction, and the submerged soils with no drainage, in general, a still smaller relative decrease.

The marked decrease in conductivity of the well drained soils and the submerged soils with drainage is due largely to loss of soluble salts in the drainage. Although this loss was undoubtedly greater with the submerged soils with drainage than with the well drained soils the conductances of the submerged soils with drainage are higher than the values for the well drained soils because of the compensating effect of soluble iron and manganese compounds.

Among the well drained soils, conductances at the second sampling increase progressively with pH. Table 10 of Appendix shows that the higher conductances are associated with higher concentrations of nitrate. The submerged soils with drainage exhibit a similar trend but for a different reason -- because of an increase in concentration of iron and manganese, as the same table indicates. There is no such regularity in the behavior of the submerged soils with no drainage but there is a suggestion of greater decreases in conductances with increase in oat straw content.

At the third sampling; i.e., after thirty-four days from the start, the well drained soils register a further decrease in conductance, the decrease being most marked in the pH 4.9 treatments. But at all three pH levels the magnitude of the drop in conductance increases with oat straw content. This suggests that immobilization of nitrogen was active at this stage. The submerged soils with drainage show no marked deviations from the values at the previous sampling, indicating that a sort of steady state has been attained, in which release of substances from the solid phase is probably balancing losses, chiefly in the drainage. The submerged soils with no drainage, without exception, show marked decreases -- decreases which are most pronounced at the two higher pH levels. The concomitant decline in nitrate concentrations at the high pH values suggests the reason for the marked decrease in conductance.

The values for conductance at the final sampling, 108 days from start, show in a striking manner the influence of drainage on the electrolyte concentration of the submerged soils. The submerged soils with drainage, regardless of the pH and oat straw treatments, all tend to have conductances around the relatively low value of about 400 micro-mhos. The submerged soils with no drainage tend towards a figure which is about five times that for the submerged soils with drainage. Since

nitrate and sulfate are absent, the high specific conductance of the percolates from the submerged soils with no drainage may be taken as an index of a much higher concentration of reduced substances than in the soils with drainage.

A curious feature of the submerged soils with no drainage is that the conductance at the final sampling decreases with increase in oat straw content, at all three levels of pH. The chemical analyses reveal a similar trend for soluble iron and manganese. Possibly, iron and manganese are removed as insoluble complexes.

Some typical changes in conductance during the growing season are represented graphically in Figs 2. and 3. These graphs bring out dramatically the marked decrease in specific conductance with time, even in the submerged soils. The apparent contradiction to the observations and theoretical principles discussed earlier disappears when it is realized that the effects of an extraordinarily initial electrolyte content and assimilation of salts by the rice plants were superimposed on the increase in conductance associated with reduction.

4.313 Redox Potentials

The detailed results of the redox potential measurements are given in Tables 1-8 of the Appendix, along with the other analyses. Each value represents the mean of the potentials of two electrodes seated permanently at a depth of 6" in each pot.

As is to be expected from a heterogeneous system like the soil there is some variability among replicates of the same treatment. The differences are most pronounced during the first two weeks when the systems are undergoing rapid adjustment. The amplitude of the variations is much less marked in the submerged soils, especially after the initial period of rapid potential fluctuations is over.

The mean values of the potentials for each treatment are presented, along with the mean chemical and physico-chemical analyses in Tables 9-16 of the Appendix. The potentials of individual pots, corrected to pH 6 and averaged for each treatment are given in Table 3 on pages 90-91. The potentials were corrected to pH 6 because the pH values of almost all the soils, during the great part of the growing season, fell in the range 6.0 ± 1.0 . The factor 80 mv. per pH unit, obtained by Bradfield and co-workers (33) for the E_h -pH relationship of many New York soils, was used for the conversion.

The potentials reflect the treatment effects to a marked degree. The well drained soils show potentials which are much higher and vary less with time than those of the submerged soils. After a relatively small initial drop they rise sharply to the high levels characteristic of well drained soils. But even these potentials are influenced, especially in the early stages, by the pH level and

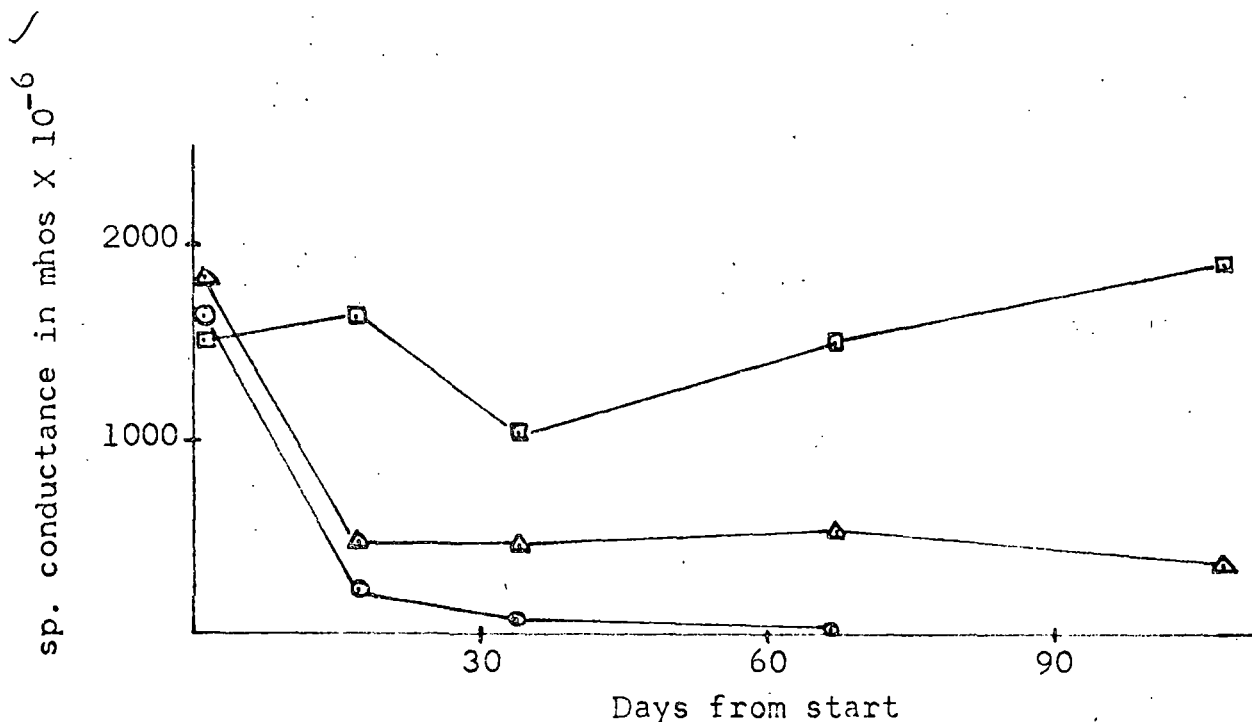


Fig. 2. Changes in specific conductance of percolates from pH 4.9, no oat straw treatments.

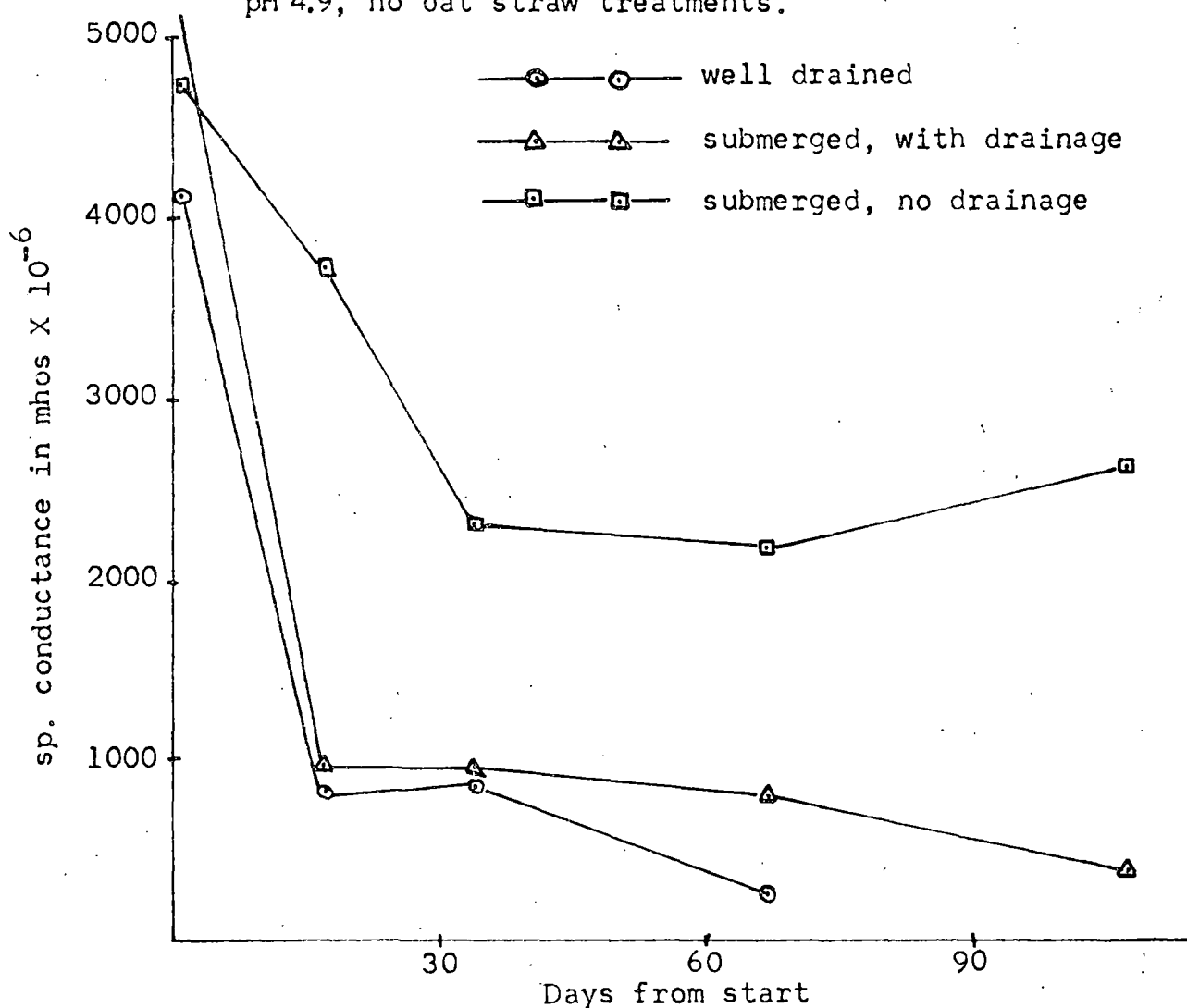


Fig. 3. Changes in specific conductance of percolates from pH 6.0, no oat straw treatments.

TABLE 3
CHANGES IN REDOX POTENTIALS OF SOILS DURING THE PERIOD OF GROWTH

Treatment No.	pH	Treatments		Redox Potential Corrected to pH 6.0 (in mv) on Days from Start									
		Oat	Drainage*	1	3	5	8	16	32	65	106		
		Straw %											
I	4.9	0.0	w.d.	530	466	447	517	559	582	565	613		
II	"	"	s.w.d.	452	-106	+210	+73	-75	-193	-197	-196		
III	"	"	s.n.d.	432	-113	+105	+13	-77	-125	-172	-172		
IV	4.9	0.2	w.d.	426	400	441	467	529	514	593	609		
V	"	"	s.w.d.	451	-309	-123	-34	-103	-168	-196	-177		
VI	"	"	s.n.d.	453	-256	-35	-41	-92	-158	-163	-170		
VII	4.9	0.4	w.d.	478	62	246	433	542	582	660	652		
VIII	"	"	s.w.d.	407	-251	-199	-70	-101	-176	-172	-183		
XIX	"	"	s.n.d.	417	-267	-260	-80	-79	-151	-161	-162		
X	5.7	0.0	w.d.	472	380	409	476	544	498	535	652		
XI	"	"	s.w.d.	430	287	251	76	-105	-185	-177	-174		
XII	"	"	s.n.d.	374	289	216	242	+124	-102	-172	-175		
XIII	5.7	0.2	w.d.	458	328	345	437	543	516	585	671		
XIV	"	"	s.w.d.	384	228	208	-20	-107	-161	-173	-191		
XV	"	"	s.n.d.	417	215	204	83	-85	-144	-118	-191		
XVI	5.7	0.4	w.d.	370	173	260	319	560	574	626	666		
XVII	"	"	s.w.d.	294	-257	-86	-104	-135	-185	-192	-175		
XVIII	"	"	s.n.d.	292	-91	-9	-75	-106	-174	-162	-164		

TABLE 3 (Continued)

Treat- ment No.	pH	Treatments		Redox Potential Corrected to pH 6.0 (in mv) on Days from Start										
		Oat Straw %	Drainage*	1	3	5	8	16	32	65	106			
XIX	6.0	0.0	w.d.	454	263	290	424	538	534	533	610			
XX	"	"	s.w.d.	456	221	195	77	- 95	-175	-140	-189			
XXI	"	"	s.n.d.	427	220	200	207	+195	- 92	-186	-180			
XXII	6.0	0.2	w.d.	495	316	317	405	538	587	571	668			
XXIII	"	"	s.w.d.	385	237	197	6	-144	-191	-173	-170			
XIV	"	"	s.n.d.	336	231	217	157	- 51	-149	-172	-174			
XXV	6.0	0.4	w.d.	312	119	166	171	537	554	551	616			
XXVI	"	"	s.w.d.	290	111	52	- 73	-134	-172	-146	-178			
XXVII	"	"	s.n.d.	277	158	121	- 7	-111	-170	-132	-170			

* w.d. = well drained; s.w.d. = submerged with drainage; s.n.d. = submerged, no drainage.

organic matter content (Vide Fig. 7). The submerged soils show a sharp drop in potential during the first few days. The magnitude of this decrease and the course the potential changes take subsequently are governed by the three treatment factors, pH, oat straw content, and drainage. The submerged soils at pH 4.9 (the unlimed soils) show a drastic drop in potential. This fall in potential is greater in the 0.2 and 0.4 percent oat straw treatments than in the no-oat-straw treatment. The lowest potential on the third day from the start was registered by the pH 4.9, 0.2 percent oat straw, submerged with drainage treatment. Despite these differences the general pattern of potential changes for the submerged soils of the pH 4.9 treatment is the same. The potential-time curves for the no-oat-straw treatment exemplify the changes. They are given in Fig. 4 along with the curve for the well drained soil.

The curves for the submerged soils bring out clearly the sharp minimum on the third day from start. This minimum was even more pronounced with the oat straw treated soils. The minimum is followed by a rapid rise to a level of about 200 mv. after which the potentials decline gradually and after 30 days get stabilized around -180 mv. There is no valid explanation for the rise in potential following the initial drop. But if the results with bacterial cultures may be extrapolated to soils this rise in potential may be attributed to the decomposition of hydrogen peroxide elaborated by aerobic organisms in the first three days of submergence. A curious feature of the potentials of the submerged soils of pH 4.9 is that the final stable potentials for the soils with drainage is consistently 10-30 mv. lower than those for the soils with no drainage. Apparently the oxygen introduced to the soil in the 0.4" of water that sank into the soil daily in the submerged soils with drainage was consumed in the upper layers of the soil.

The behavior of the submerged soils of the two higher pH treatments present a sharp contrast to that of the submerged soils at pH 4.9. First, there is no minimum; secondly, the decline in potential is more gradual especially in the case of the no oat straw, no drainage treatments; and thirdly, the influence of drainage and oat straw are much more pronounced in the early stages. These differences are brought out dramatically by a comparison of Fig. 4 with Fig. 5 or better still with Fig. 6.

Figure 5 illustrates the absence of a minimum in the potential-time curves, the slower decline in potential of the submerged soil with no drainage than in its counterpart in Fig. 4 and the marked difference between the drainage and no drainage treatments. The absence of a minimum suggests the operation of some stabilizing influence. The stabilizing influence appears to operate for a longer period in the soil with no drainage than in the one with drainage. This suggests that the factor retarding the fall in potential is a soluble substance. The chemical analyses of the percolates from these treatments (Tables 9-16 of the Appendix) reveal the presence of 263 p.p.m. nitrate N even 18 days after submergence in the percolates from the submerged no drainage treatment in question.

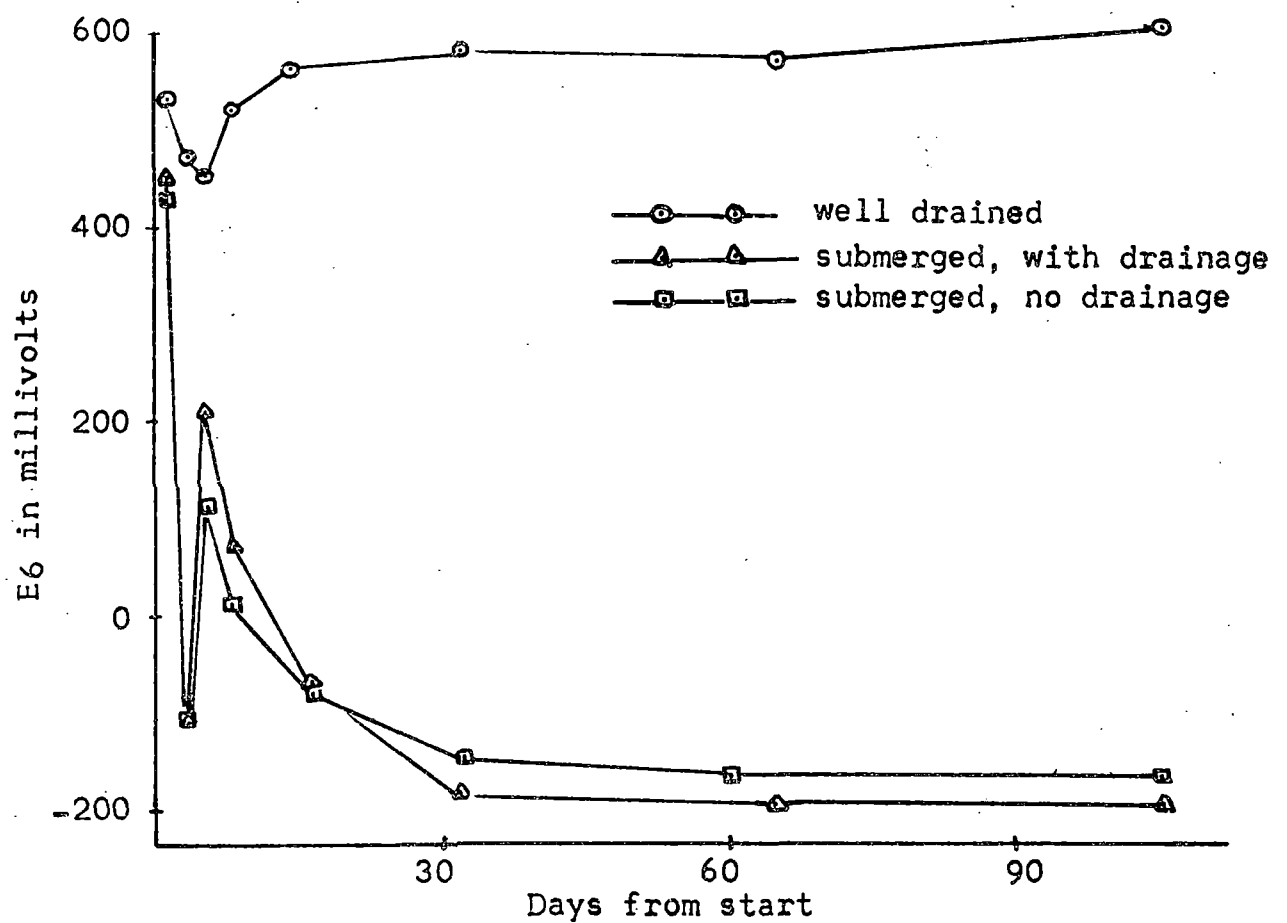


Fig. 4. Changes in Redox potential: pH 4.9, no oat straw treatment.

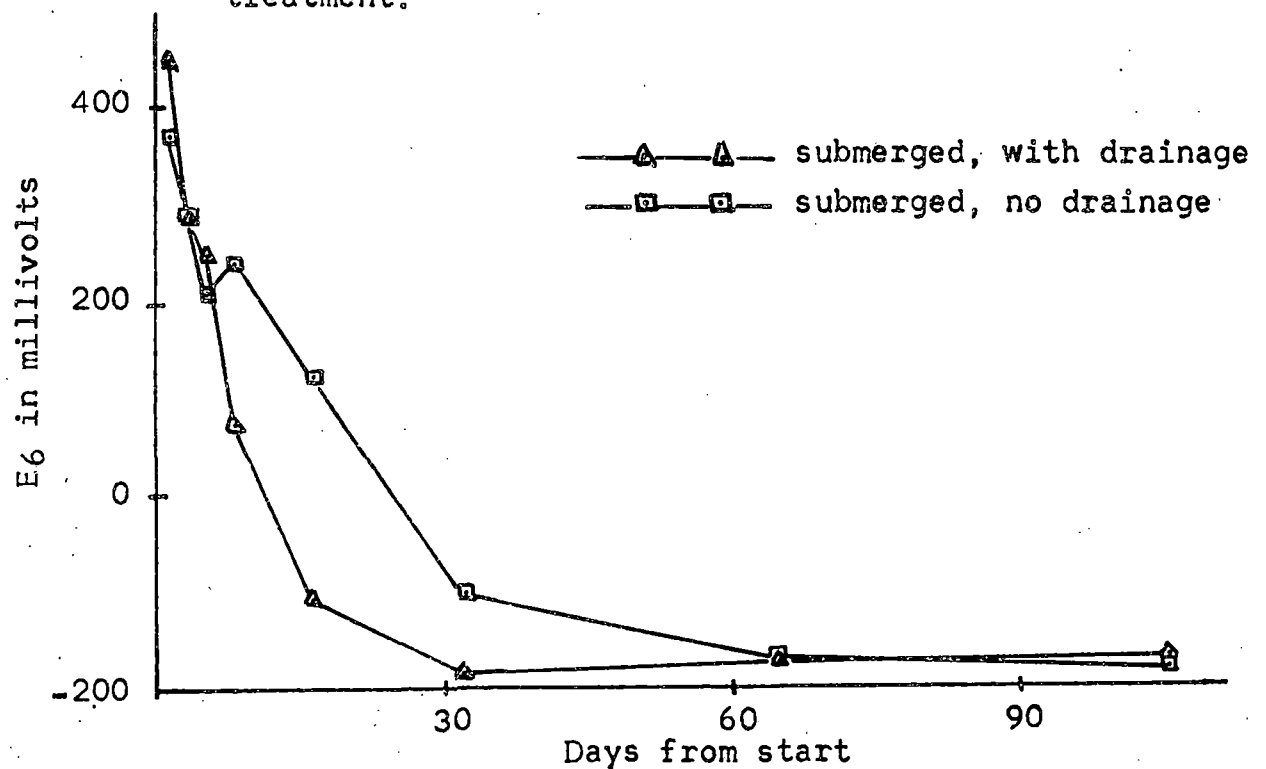


Fig. 5. Changes in Redox potential: pH 5.7, no oat straw treatment.

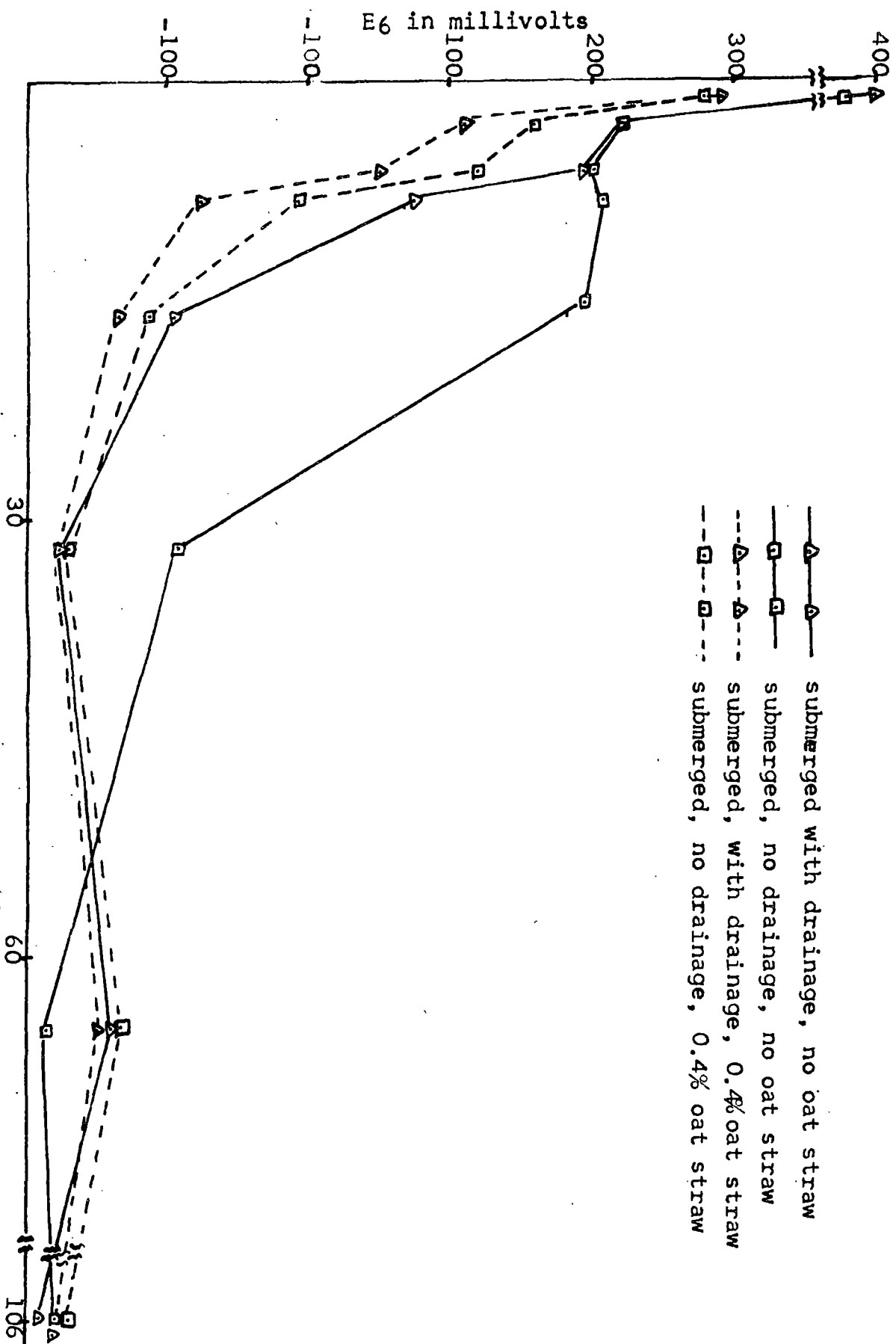


Fig. 6. Changes in Redox potential at pH 6.0 and two levels of oat straw.

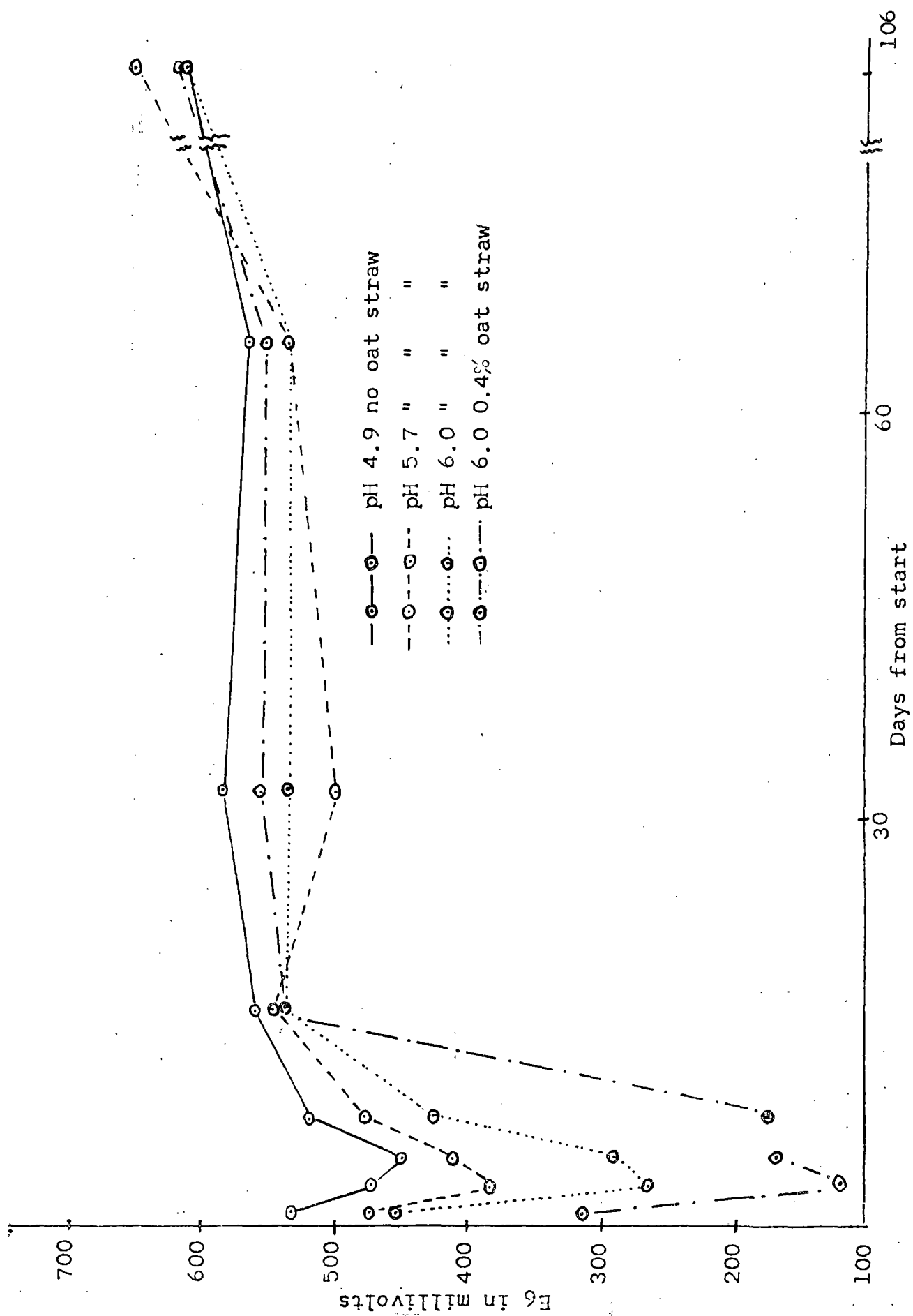


Fig. 7. Changes in Redox potential of well drained soils at three pH levels.

Figure 6 brings out even more clearly the stabilizing effect of nitrate on the redox potential. The potential remains at the level of 200 mv. longest in the no oat straw, no drainage treatment, less so in the no oat straw, with drainage treatment, and least of all in the 0.4 percent oat straw, drainage treatment. The changes in nitrate concentrations are generally in line with these observations as Tables 9-16 of the Appendix indicate. Thus changes in redox potential in these soils in the early stages are governed by the factors that control the nitrate concentration.

At the end of 106 days the potentials of the submerged soils at pH 5.7 and 6.0 all approached a value of approximately -180 mv. at pH 6.

The significant conclusions from this study are (i) the presence of nitrate retards the onset of reducing conditions; (ii) drainage in submerged soils, contrary to expectation and to popular belief, increases the rate and intensity of reduction, especially in the early stages; (iii) the presence of organic matter accelerates the reduction process; and, (iv) the potential of a submerged soil at the end of three months is of the order of -200 mv. at pH 6 and is independent of pH, organic matter levels at the start, and the presence or absence of a moderate amount of drainage.

4.32 Chemical Analyses

4.321 Percolates

Iron. The detailed results of the iron analyses of the percolates on the several sampling dates are given in Tables 1-5 of the Appendix under "Analyses of Percolates." The mean analyses for each treatment are presented, along with the other chemical analyses, in Tables 9-13, also of the Appendix. These mean values are reproduced in Table 4 for easy reference.

The three treatment factors, pH, drainage, and organic matter level, have all had a profound effect on the concentration of iron in the soil solution. But the most conspicuous changes are associated with the drainage treatments.

The well drained soils, regardless of the pH and organic matter levels, have iron concentrations which are insignificant in comparison with those of the submerged soils. The slight variations they show at the different pH and organic matter levels have little meaning in the face of the considerable experimental error involved in the determination of such small amounts of iron. The well drained soils are therefore omitted in the graphic representation, in Figures 8 and 9, of the changes in iron concentration during the growing season. Also no further reference will be made to them in this section.

TABLE 4
CHANGES IN CONCENTRATION OF IRON
DURING THE PERIOD OF GROWTH

Treat- ment No.	Treatment			Fe in p.p.m. in Percolates on Days from Start				
	pH	Oat Straw %	Drainage	1	17	34	67	108
I	4.9	0.0	w.d.	0.22	0.1	0.2	0.1	-
II	"	"	s.w.d.	0.54	44.5	114	164	132
III	"	"	s.n.d.	0.18	35.8	81.6	354	561
IV	4.9	0.2	w.d.	-	0.1	0.1	0.1	-
V	"	"	s.w.d.	0.74	44.5	157	155	110
VI	"	"	s.n.d.	0.54	88.3	207	435	542
VII	4.9	0.4	w.d.	-	0.06	0.1	0.1	-
VIII	"	"	s.w.d.	0.88	82.8	118	170	119
IX	"	"	s.n.d.	0.88	114.0	240	474	360
X	5.7	0.0	w.d.	0.10	0.02	0.1	0.1	-
XI	"	"	s.w.d.	0.14	19.6	101	120	89.7
XII	"	"	s.n.d.	0.21	3.3	8.2	96.7	191
XIII	5.7	0.2	w.d.	0.18	0.1	0.1	0.1	-
XIV	"	"	s.w.d.	0.23	72.7	90	124	91.3
XV	"	"	s.n.d.	0.17	11.3	63.5	150	148
XVI	5.7	0.4	w.d.	0.35	0.1	0.1	0.1	-
XVII	"	"	s.w.d.	0.40	96.8	96.0	105	91.0
XVIII	"	"	s.n.d.	0.59	39.7	167	180	179
XIX	6.0	0.0	w.d.	0.11	0.1	0.1	0.1	-
XX	"	"	s.w.d.	0.11	25.7	76.0	109	90.3
XXI	"	"	s.n.d.	0.08	3.2	20.5	80	168
XXII	6.0	0.2	w.d.	0.18	0.3	0.1	0.1	-
XXIII	"	"	s.w.d.	0.15	70.8	78	125	102
XXIV	"	"	s.n.d.	0.12	19.2	78	148	126
XXV	6.0	0.4	w.d.	0.36	0.1	0.1	0.1	-
XXVI	"	"	s.w.d.	1.40	73.1	80.0	120	61.3
XXVII	"	"	s.n.d.	1.40	26.0	133	147	122

In the case of the submerged soils, the concentration of iron in the soil solution is determined largely by the presence or absence of drainage. This is especially true of the pH 5.7 and 6.0 treatments in the early stages of submergence and of the pH 4.9 treatment in the later stages.

In the pH 5.7 and 6.0 treatments, drainage accentuates the increase in iron concentration in the early stages of submergence. The figures for the second sampling, in Table 4, show that the concentration of iron in the submerged soils with drainage is several times that of the corresponding soils with no drainage. The ratio is narrowed as the oat straw level increases. Table 9 of the Appendix reveals that the lower content of iron in the submerged soils without drainage than in the submerged soils with drainage is associated with a higher content of nitrate.

In the pH 4.9 treatment the effect of drainage is the reverse: the submerged soils with no drainage have a higher content of soluble iron than the corresponding submerged soils with drainage. The exceptional behavior of the no-oat-straw, submerged, no-drainage treatment may be attributed to the retardation of reduction by nitrate, which for reasons that are not clear, was present in high concentration at this time. (v. analyses for pot no. 8, Table 10 of Appendix.) But the effect of increasing the oat straw level is to increase the concentration of iron in the solution of the submerged soils, as in the other two pH treatments. The behavior of these soils is easily explained. The soils of this pH treatment all started with a low nitrate content. (v. Tables 1 and 9 of the Appendix.) On submergence the reduction proceeded without any impedance. Thus the soils with no drainage built up high concentrations of iron, especially in the oat straw treatments. The removal of iron in the drainage accounts for the lower concentration of iron in the treatments with drainage. The subsequent behavior of the submerged soils of the pH 4.9 treatment which is brought out clearly in Fig. 8 may be interpreted on the same lines. The submerged soils with no drainage build up concentrations of iron according to the intensity of the reduction process while the submerged soils with drainage have differences due to organic matter level ironed out and tend towards a common level for their soluble iron concentrations. The effect of drainage in the pH 4.9 treatment is thus to nullify the influence of organic matter and to prevent the build up of a high concentration of iron in the solution.

The behavior of the pH 5.7 and 6.0 treatments after the exhaustion of the nitrate supply is similar: the no-drainage treatments build up iron concentrations according to the level of organic matter while the drainage treatments regardless of the organic matter levels tend towards a common iron concentration as Fig. 9 (a) and (b) indicate.

The pH level also has had a marked effect on the changes in iron concentration in the percolates. This is evident even in the

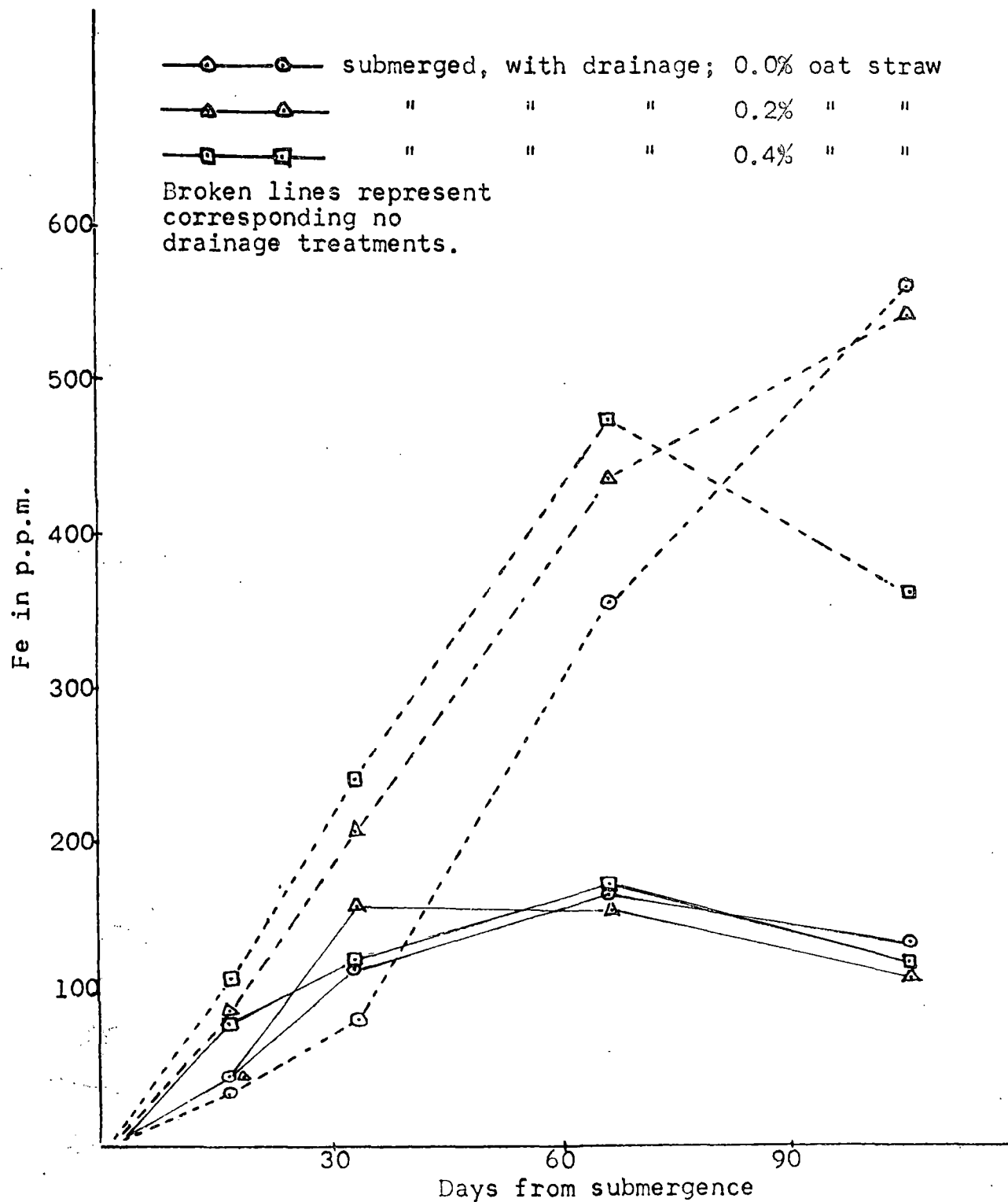


Fig. 8. Changes in concentration of Iron in percolates from pH 4.9 treatments.

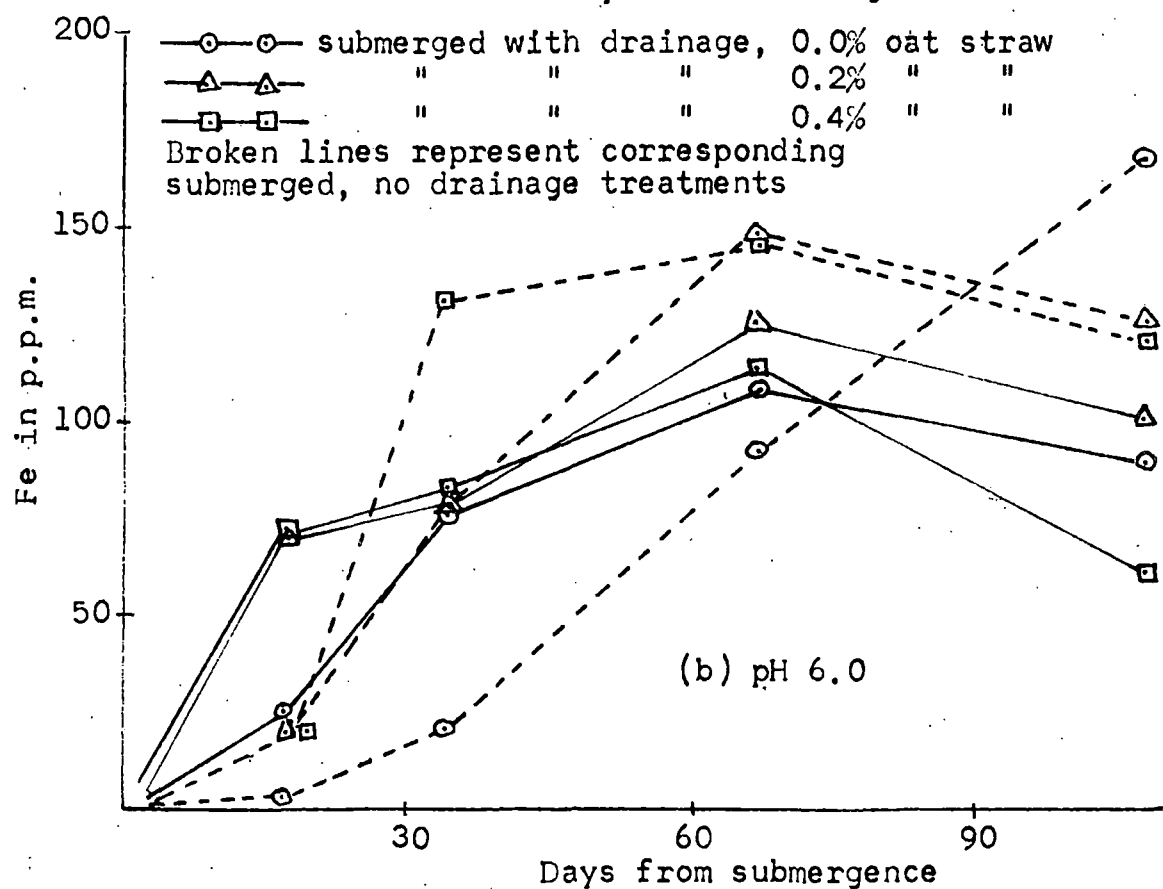
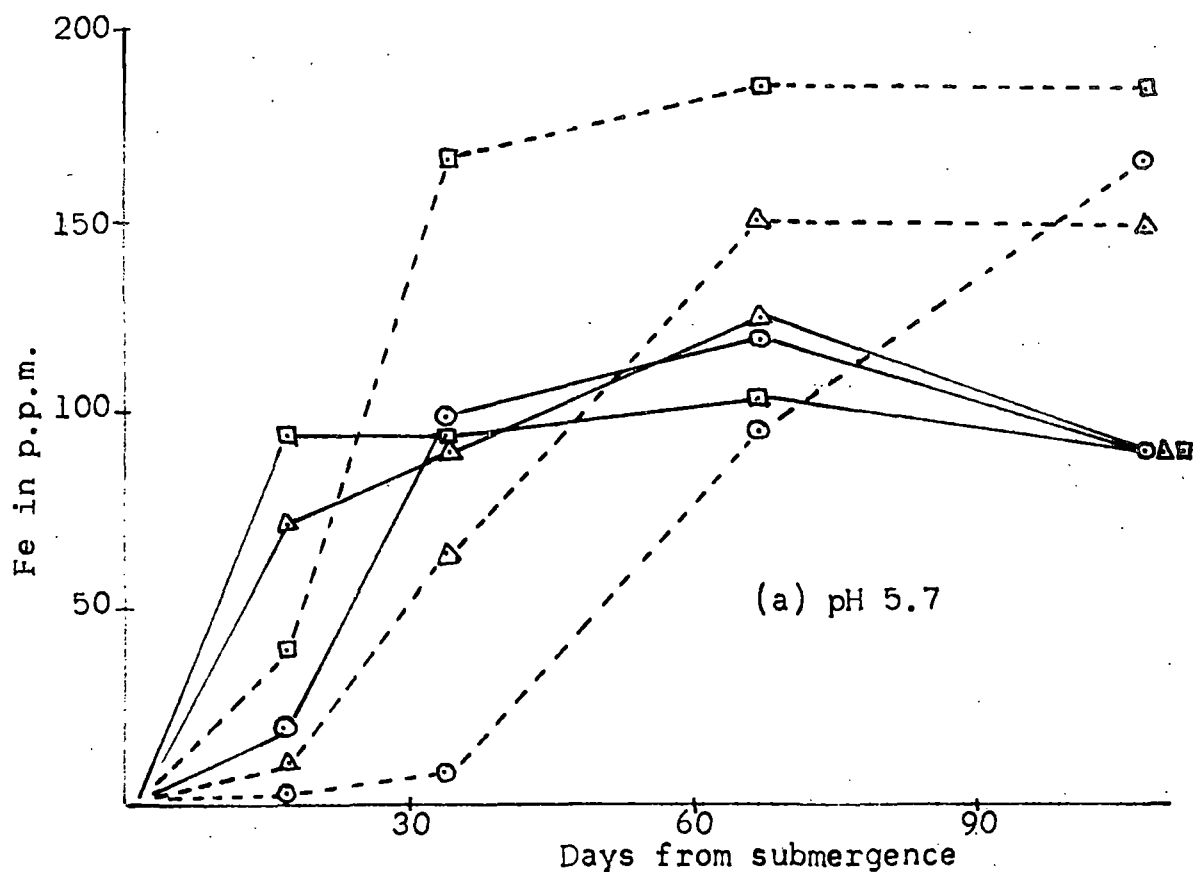


Fig. 9. Changes in concentration of Fe in percolates at pH 5.7 and 6.0.

case of the submerged soils with drainage where treatment differences, as already indicated, tend to be eliminated. Throughout the growing season the concentration of iron in these treatments is highest in the pH 4.9 treatment while the differences between the pH 5.7 and 6.0 treatments are not appreciable. But the differences due to pH treatments are most remarkable in the no-drainage treatments. At pH 4.9, the iron concentration increases at a rapid rate, as Fig. 8 indicates, and in the no-oat-straw treatment reaches the astonishing level of 561 p.p.m. Thus during the greater part of the growing season the rice plants of the pH 4.9, submerged, no-drainage treatments are subjected to an extraordinarily high concentration of iron.

The behavior of the pH 5.7 and 6.0 submerged, no-drainage treatments is markedly different from those of pH 4.9. The iron concentration is comparatively small in the early stages and never rises to excessive heights at any stage of the experiment. In fact the maximum concentration attained by any treatment is only 180 p.p.m. compared with the 561 p.p.m. for the pH 4.9 treatments. Between pH 5.7 and pH 6.0 the differences are not marked although Table 4 clearly shows that the concentrations at pH 5.7 are throughout the season greater than at pH 6.0.

The results of the addition of oat straw are interesting. In the early stages, the effect of increasing the level of oat straw is, without exception, to increase the concentration of iron. The effect is most marked in the no-drainage pH 4.9 treatments and is exemplified by the figures for the second and third sampling, in Table 4. It is also evident from Fig. 8. But in the later stages the iron concentrations of the oat straw treatments, at all pH levels, show a curious tendency to decrease. In sharp contrast to this behavior, the iron concentrations of the no-oat-straw treatments increase slowly at the start and then at an increasingly rapid rate until at the final sampling they equal and even exceed the concentrations of the corresponding oat straw treatments. Figures 8 and 9 show the striking similarity of the course of changes in iron concentration for the no-oat-straw, no-drainage treatments at all three pH levels. The more rapid increase in iron concentration in the oat straw treatments than in the no-oat-straw treatments, in the early stages of submergence, is quite intelligible. But the explanation of the tendency of the iron concentrations of the oat straw treatments to be stationary or even to decrease while those of the no-oat-straw treatments to increase rapidly, in the later stages, can be only speculative.

The iron in solution comprises (i) ionic Fe^{+2} and (ii) iron in the form of complexes. The concentration of ionic Fe^{+2} is determined by pH. This alone explains why it is highest in the pH 4.9, and lowest in the pH 6.0 treatments, especially in the early stages before appreciable increases in pH had taken place. But the concentrations of iron at all three pH levels are considerably in excess of those permitted by the relationship: $\text{pFe}^{+2} = 2\text{pH} + 1.93 - .25 \text{pO}_2$. Obviously a high proportion of the iron is present in the form of

soluble complexes. Now, of the complexing agents present in a submerged soil, lactic acid is probably the most abundant. But lactic acid, as already indicated, is rather short lived for it is attacked by bacteria with formation of butyric and propionic acids. With the destruction of the lactic acid the iron concentration will tend towards the lower levels permitted by ionic equilibria. The progressive increase in the iron concentration in the no-oat-straw treatments may be attributed to the release of the latent capacity of the soils to undergo reduction, by the disappearance of nitrate.

The conclusions from this study may be summarized as follows: (i) submergence causes a tremendous increase in the concentration of soluble iron; (ii) the iron concentrations are not static; (iii) the highest concentrations of iron during the greater part of the season are associated with the low pH, submerged, no-drainage treatments; (iv) drainage tends to nullify the effect of pH and organic matter on the iron concentration; (v) the presence of nitrate markedly retards the reduction of iron; (vi) with a vertical drainage rate of 0.4" a day about 600 lbs. of iron per acre may be lost from a submerged soil during a single season.

Manganese. The changes in soluble manganese follow the same general pattern as those of iron. The influence of three factors pH, oat straw, and drainage levels show the expected parallelism.

The well drained soils are, except at the very start, extremely low in soluble manganese and no differences due to pH and organic matter treatments are perceptible.

In the case of the submerged soils, pH, organic matter, and the presence or absence of drainage have all had a marked effect as the figures in Table 5 indicate. Of these factors, apparently, the drainage has had the most pronounced effect.

In the early stages, as with iron, the concentration of manganese is greater in the soils with drainage than in the soils without drainage in the pH 5.7 and 6.0 treatments while in the pH 4.9 treatments the situation is just the reverse. With the disappearance of nitrate from the soils at pH 5.7 and 6.0, all three pH treatments show the same trends: the concentration is higher in the no-drainage than in the drainage treatments, and increases with time. The soils with drainage all tend to become lower and lower in soluble manganese until at the final sampling 108 days after submergence their manganese concentrations attain the relatively low level (for a submerged soil) of about 10 p.p.m. in the soil solution. These trends are brought out clearly in Fig. 10.

The effect of pH level, though clearly discernible, is not as marked as in the case of iron. The highest concentrations of soluble manganese during the greater part of the growing season are associated with the submerged no-drainage, pH 4.9 treatments and was only 87.7 p.p.m.

TABLE 5
CHANGES IN CONCENTRATION OF MANGANESE
DURING THE PERIOD OF GROWTH

Treatment No.	Treatment			Mn in p.p.m. of Percolate on Days from Start				
	pH	Oat Straw %	Drainage	1	17	34	67	108
I	4.9	0.0	w.d.	7.6	0.8	0.4	0.1	-
II	"	"	s.w.d.	7.7	11.6	17.0	16.4	10.7
III	"	"	s.n.d.	5.5	23.0	20.7	41.9	87.7
IV	4.9	0.2	w.d.	-	0.8	0.1	0.1	-
V	"	"	s.w.d.	6.9	11.8	20.0	14.8	9.0
VI	"	"	s.n.d.	7.9	30.8	35.4	56.5	70.8
VII	4.9	0.4	w.d.	-	2.9	0.1	0.1	-
VIII	"	"	s.w.d.	8.8	20.9	20.3	16.6	8.2
IX	"	"	s.n.d.	11.5	37.9	45.3	55.0	41.0
X	5.7	0.0	w.d.	1.4	0.1	0.1	0.1	-
XI	"	"	s.w.d.	1.5	12.6	25.4	18.5	12.2
XII	"	"	s.n.d.	1.5	7.6	19.0	27.4	46.7
XIII	5.7	0.2	w.d.	1.0	0.2	0.1	0.1	-
XIV	"	"	s.w.d.	0.1	23.4	20.8	16.6	10.3
XV	"	"	s.n.d.	1.7	9.7	24.7	29.0	29.9
XVI	5.7	0.4	w.d.	1.3	0.3	0.1	0.1	-
XVII	"	"	s.w.d.	1.5	29.1	20.9	13.5	9.9
XVIII	"	"	s.n.d.	1.4	20.9	45.7	39.6	34.1
XIX	6.0	0.0	w.d.	0.1	0.1	0.1	0.1	-
XX	"	"	s.w.d.	-	11.7	20.6	19.9	12.0
XXI	"	"	s.n.d.	0.1	7.2	22.1	32.3	44.4
XXII	6.0	0.2	w.d.	1.6	0.1	0.1	0.1	-
XXIII	"	"	s.w.d.	2.9	30.9	19.2	20.7	13.7
XXIV	"	"	s.n.d.	0.3	8.8	30.2	25.5	32.8
XXV	6.0	0.4	w.d.	1.1	0.1	0.1	0.1	-
XXVI	"	"	s.w.d.	1.1	23.4	19.5	18.4	8.5
XXVII	"	"	s.n.d.	0.1	12.9	31.3	41.0	41.8

compared with the 561 p.p.m. of iron for the same treatment at the same sampling.

The influence of oat straw levels is most marked in the submerged, no-drainage treatments and is illustrated in Fig. 10. As with iron, oat straw causes a marked increase in the concentration of manganese in the early and middle stages. Towards the end there is a tendency for the reduction process to spend itself out and for the soluble manganese concentrations to decrease in the high oat straw treatments.

There is a high degree of association between the iron and manganese concentrations of the percolates on each of the sampling dates except the first. The relationship between the iron manganese for the submerged soils at the second sampling can be described by regression equation:

$$Y = 3.59 X - 16.5$$

$$r = 0.911^{**}$$

Where Y = conc. of soluble iron in p.p.m. of percolate and X = conc. of soluble manganese in p.p.m. of percolate. This high correlation is obtained despite the unusual behavior of those treatments with a high nitrate content. In these treatments the concentration of manganese was higher than that of iron although according to the over-all relationship given the iron concentration not only exceeds the manganese but does so by an appreciable factor. The influence of the nitrate content on the Fe:Mn ratio is illustrated by the figures in Table 6. These figures show that even within a given treatment Fe:Mn ratio is strongly influenced by the presence of nitrate.

The narrowing and even inversion of the Fe:Mn ratio when nitrates are present indicates a preferential reduction of manganic compounds. This is in complete agreement with the theoretical principles discussed in an earlier section. The standard oxidation-reduction potentials (in volts) corrected to pH 7.0 are 0.43 for the $\text{MnO}_2 - \text{Mn}^{+2}$ system, 0.41 for the $\text{NO}_3 - \text{NO}_2$ system and - 0.10 for the $\text{Fe}(\text{OH})_3 - \text{Fe}^{+2}$ system. Thus so long as nitrates are present in large amounts no appreciable reduction of iron could occur. The only restriction on the rate of reduction of manganese is the rate of solution of MnO_2 .

The same general parallelism is noticeable between the iron and manganese concentrations at the third sampling but the degree of association has been reduced and the Fe:Mn ratio widened. The regression of iron on manganese in the percolates from the submerged pots is given by the expression

$$Y = 5.00 X - 24.5$$

$$r = 0.730^{**}$$

As inspection of the Fe and Mn columns of Table 3 of Appendix reveals that the Fe:Mn ratio is widest in the pH 4.9 treatments. At the higher pH levels the value of the ratio is governed by the presence or absence of nitrate.

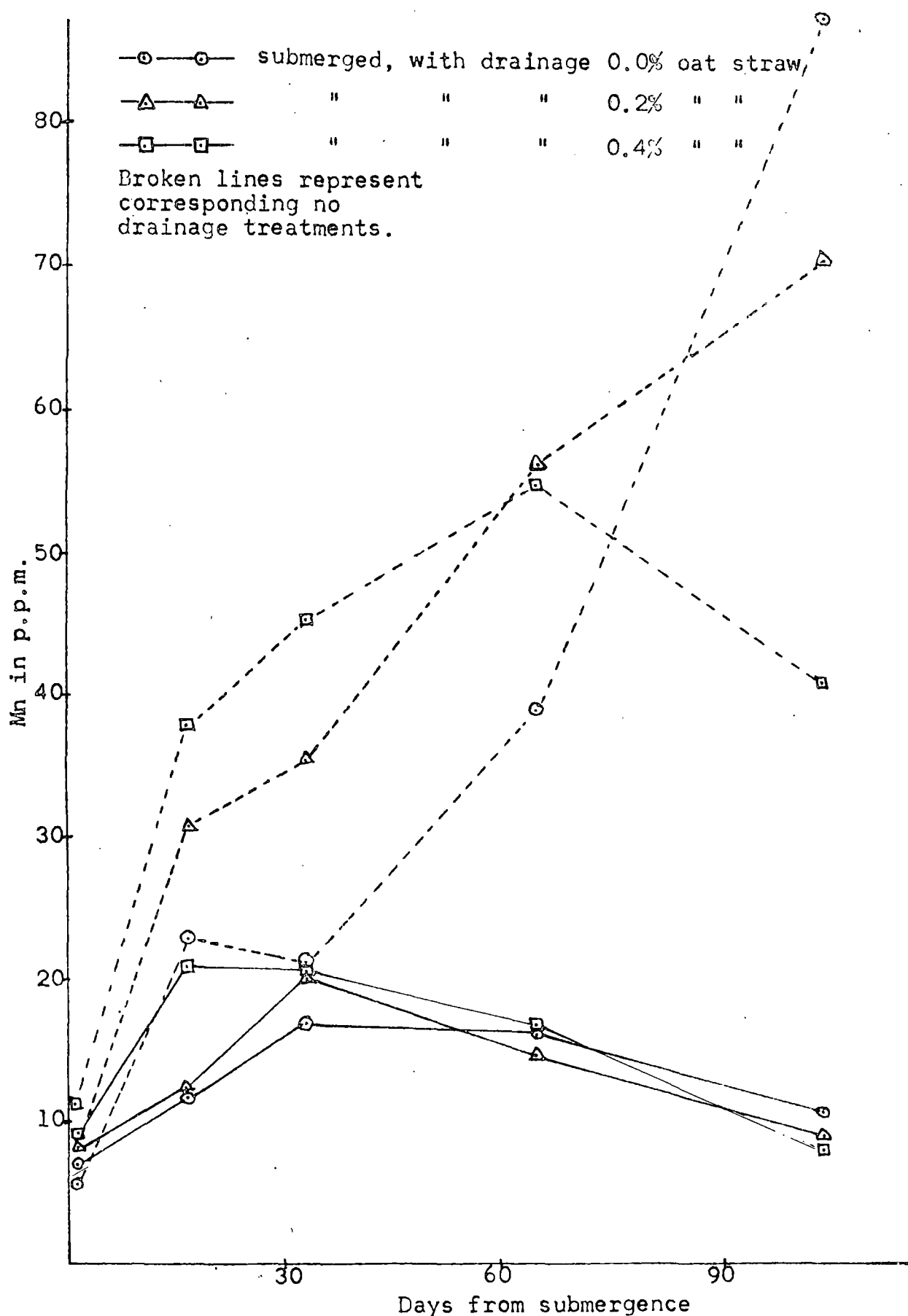


Fig. 10. Changes in concentration of Manganese in percolates from pH 4.9 treatments.

TABLE 6

THE INFLUENCE ON NITRATE CONTENT ON THE Fe:Mn RATIO,
IN PERCOLATES SAMPLED 18 DAYS AFTER SUBMERGENCE

pH	Treatment		Rep.	Pot No.	Fe	Mn p.p.m.	NO ₃	Fe:Mn Ratio
	Oat Straw %	Drainage						
4.9	0.0	s.w.d.	1	4	-	-	-	-
			2	5	36.5	11.3	9.0	3.23
			3	6	52.5	11.9	0.6	4.45
4.9	0.0	s.n.d.	1	7	43.0	22.3	0.5	1.88
			2	8	5.5	18.4	90.0	0.30
			3	9	59.0	28.2	0.8	2.09
4.9	0.4	s.w.d.	1	22	89.0	22.4	0.7	3.98
			2	23	72.0	18.4	0.7	3.91
			3	24	87.5	21.8	0.7	4.01
4.9	0.4	s.n.d.	1	25	50.0	27.1	87.5	1.85
			2	26	135	35.0	1.2	3.86
			3	27	157	51.5	2.0	2.94

At the next sampling the Fe:Mn ratio is widened further as the new equation for the regression of Fe on Mn suggests:

$$Y = 6.63 X - 6.9$$

$$r = 0.756^{**}$$

At the final sampling the ratio has increased still further and has attained a value exceeding 10, uniformly.

The widening of the Fe:Mn ratio as the reduction proceeds indicates that proportionately more iron is reduced than manganese. Since manganese is reduced far more readily and is more soluble than iron the only explanation of the widening of the ratio is that the supply of reducible manganese becomes limiting.

The influence of three factors, pH, drainage and organic matter levels on the course of manganese reduction is the same as for iron. The additional points that must be stressed are: (i) the Fe:Mn ratio widens as reduction proceeds; (ii) nitrate tends to keep the Fe:Mn ratio at a low level; (iii) the loss of manganese from a submerged soil with 0.4" of vertical drainage is of the order of 70 lbs. per acre per season.

Oxidizable matter. Oxidizable matter follows a course which is roughly parallel to that of iron and manganese. The mean values for each treatment are given in Table 7.

The figures for oxidizable matter at the first sampling reflect the content of readily oxidizable organic matter. The increase of oxidizable matter with increase in oat straw content is understood in the light of Bloomfield's (25) observation that extracts of dried grass had reducing properties even under aseptic conditions. It will be recalled that the soluble iron and manganese contents of even the well drained soils at the first sampling were not insignificant.

By the second sampling the oxidizable matter contents of the well drained soils are reduced considerably while those of the submerged soils have increased. It is remarkable that despite the removal of 0.4" daily in the drainage the submerged soils with drainage had, with a single exception, a higher content of oxidizable matter than the submerged soils without drainage.

The subsequent course of oxidizable matter is erratic except in the case of the submerged soils with drainage. In these soils the content of oxidizable matter, after the initial rise, decreases progressively until at the final sampling the influence of pH and organic matter levels is hardly discernible. The convergence of the concentrations of oxidizable matter to a common level is clearly illustrated in Fig. 11. This is the exactly analogous to the behavior of iron and manganese.

The other parallelism is in regard to the influence of nitrate. Table 2 of Appendix shows that in replicates of any given treatment a high nitrate content is associated with a comparatively low oxidizable

TABLE 7

CHANGES IN OXIDIZABLE MATTER
DURING THE PERIOD OF GROWTH

Treatment No.	pH	Treatment		Ml. of 0.01 N KMnO_4 per 10 ml. of Percolate on Days from Start				
		Oat Straw %	Drainage	1	17	34	67	108
I	4.9	0.0	w.d.	4.2	0.7	1.0	1.1	-
II	"	"	s.w.d.	5.0	8.7	19.0	13.5	9.3
III	"	"	s.n.d.	3.8	7.1	17.0	58.3	77.7
IV	4.9	0.2	w.d.	-	0.6	0.6	0.5	-
V	"	"	s.w.d.	6.8	10.5	22.6	12.8	6.8
VI	"	"	s.n.d.	6.3	8.7	22.5	50.8	85.0
VII	4.9	0.4	w.d.	9.6	0.9	0.6	0.5	-
VIII	"	"	s.w.d.	14.1	11.9	23.7	13.9	6.8
IX	"	"	s.n.d.	17.1	13.8	27.6	41.3	62.0
X	5.7	0.0	w.d.	4.1	0.9	2.4	2.5	-
XI	"	"	s.w.d.	4.1	12.9	19.9	9.2	7.3
XII	"	"	s.n.d.	4.7	7.5	17.8	64.0	70.7
XIII	5.7	0.2	w.d.	6.6	1.0	1.7	0.7	-
XIV	"	"	s.w.d.	5.1	17.5	16.5	9.7	6.5
XV	"	"	s.n.d.	6.5	11.2	22.1	47.5	84.7
XVI	5.7	0.4	w.d.	8.1	1.0	1.3	0.8	-
XVII	"	"	s.w.d.	6.7	19.8	15.9	9.1	6.3
XVIII	"	"	s.n.d.	9.2	17.1	31.0	47.2	100.3
XIX	6.0	0.0	w.d.	5.4	1.7	2.9	1.3	-
XX	"	"	s.w.d.	6.5	15.4	17.5	9.5	6.1
XXI	"	"	s.n.d.	5.7	11.3	27.8	75.7	75.8
XXII	6.0	0.2	w.d.	7.6	2.1	2.3	0.8	-
XXIII	"	"	s.w.d.	7.8	16.5	15.3	9.6	7.5
XXIV	"	"	s.n.d.	6.7	15.6	26.0	64.3	77.0
XXV	6.0	0.4	w.d.	9.8	2.7	2.2	1.4	-
XXVI	"	"	s.w.d.	12.1	18.7	17.6	11.4	5.0
XXVII	"	"	s.n.d.	12.0	19.8	25.3	31.5	84.3

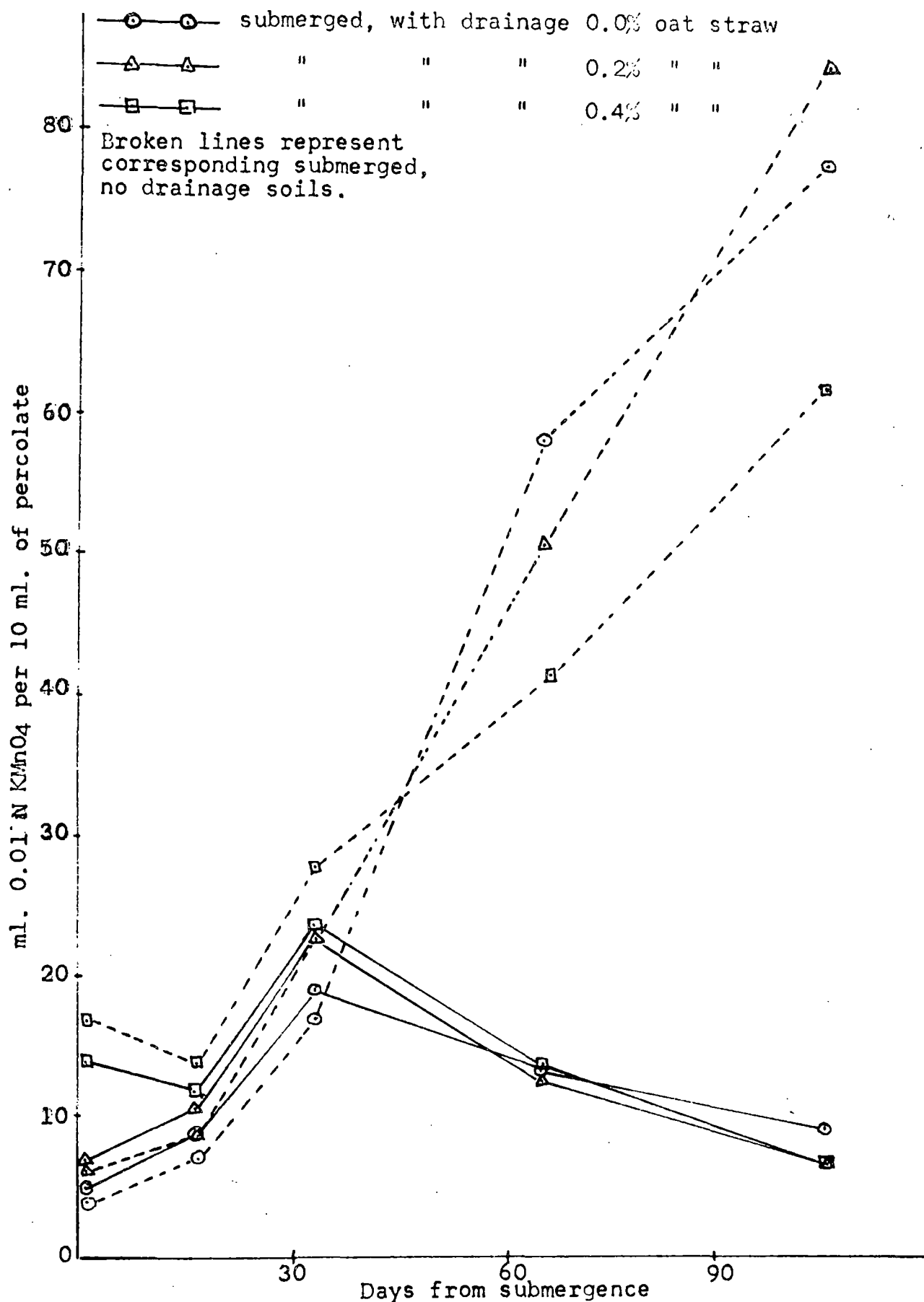


Fig. 11. Changes in concentration of oxidizable matter in percolates from pH 4.9 treatments.

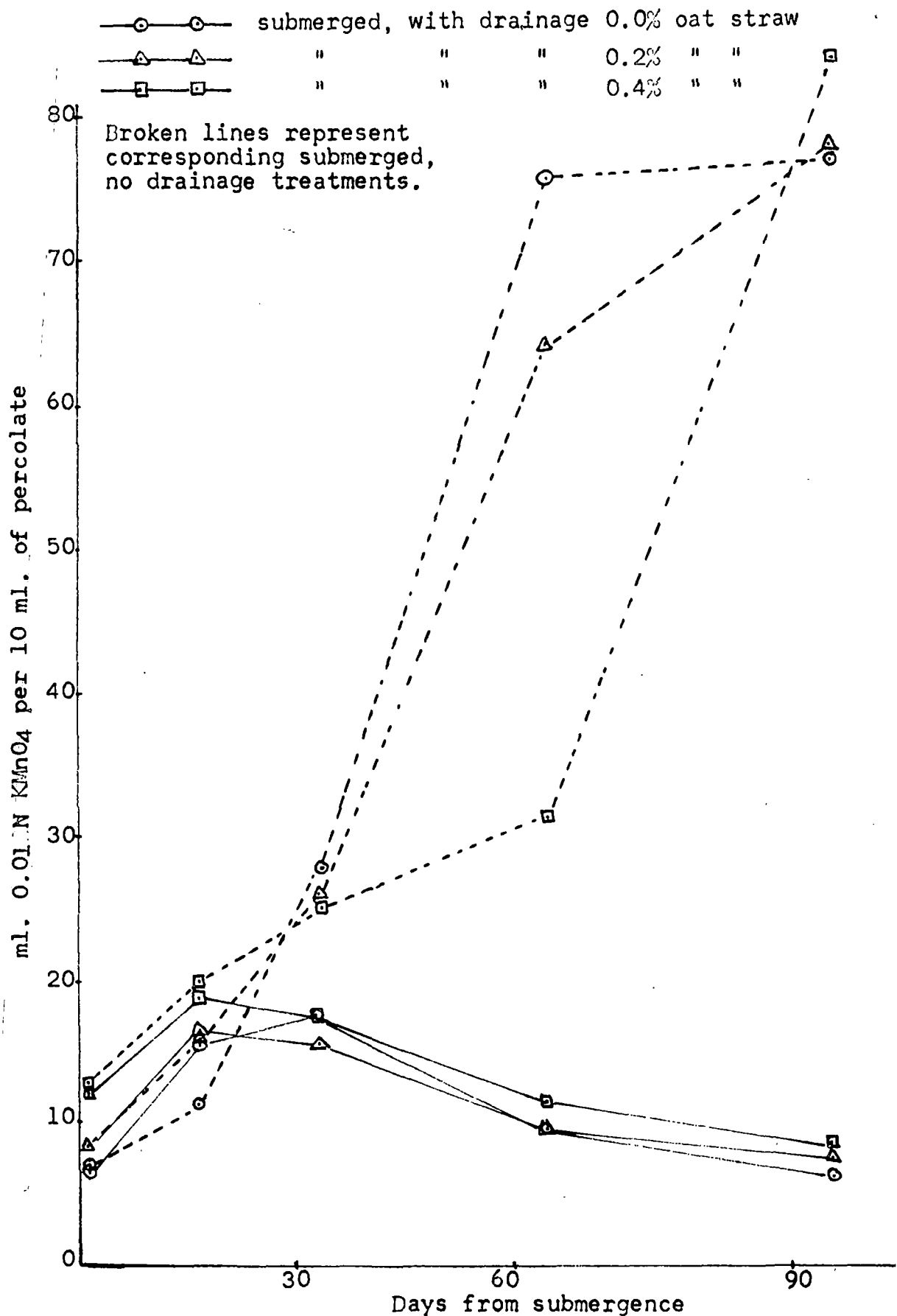


Fig. 12. Changes in concentration of oxidizable matter in percolates from pH 6.0 treatments.

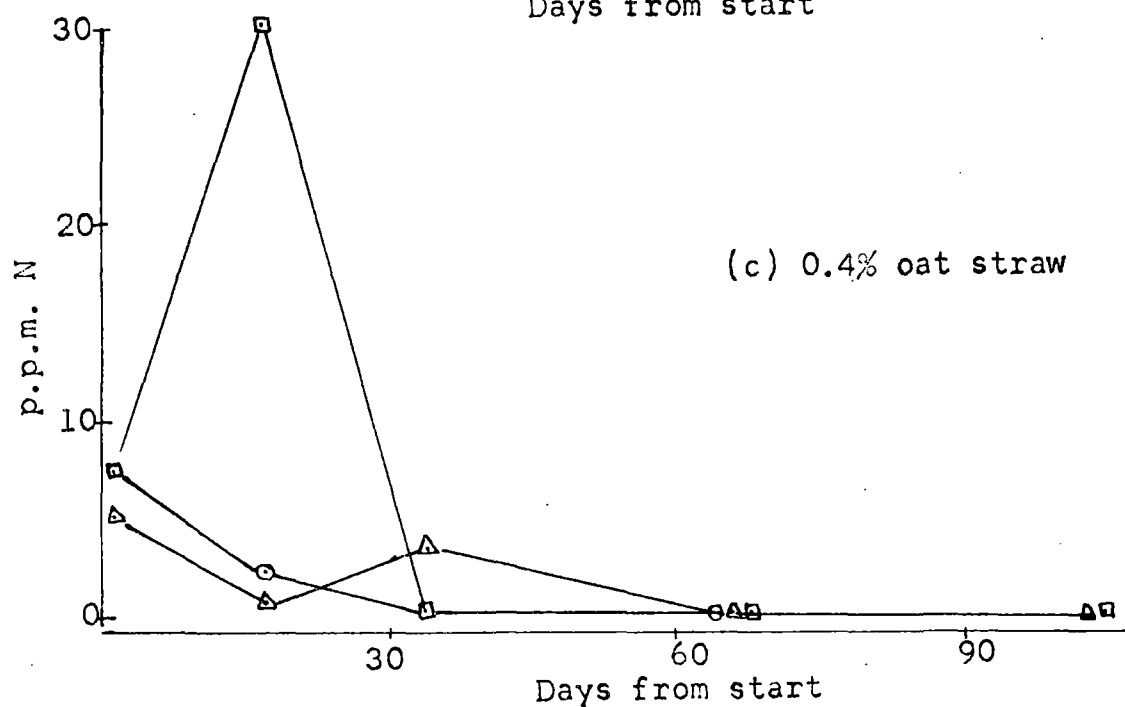
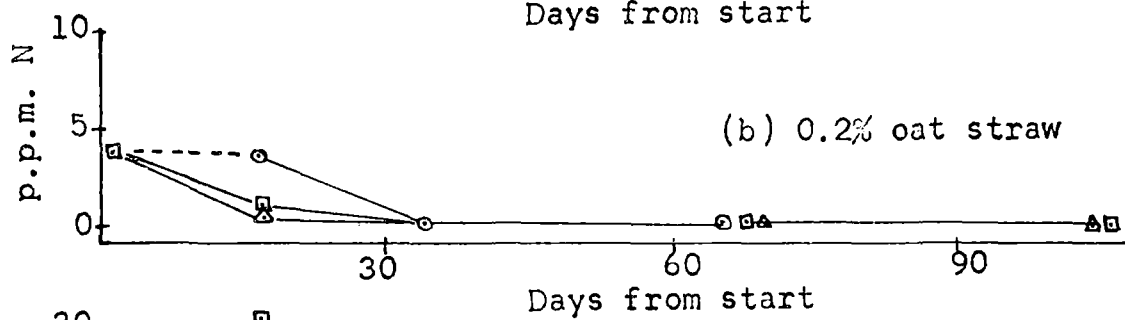
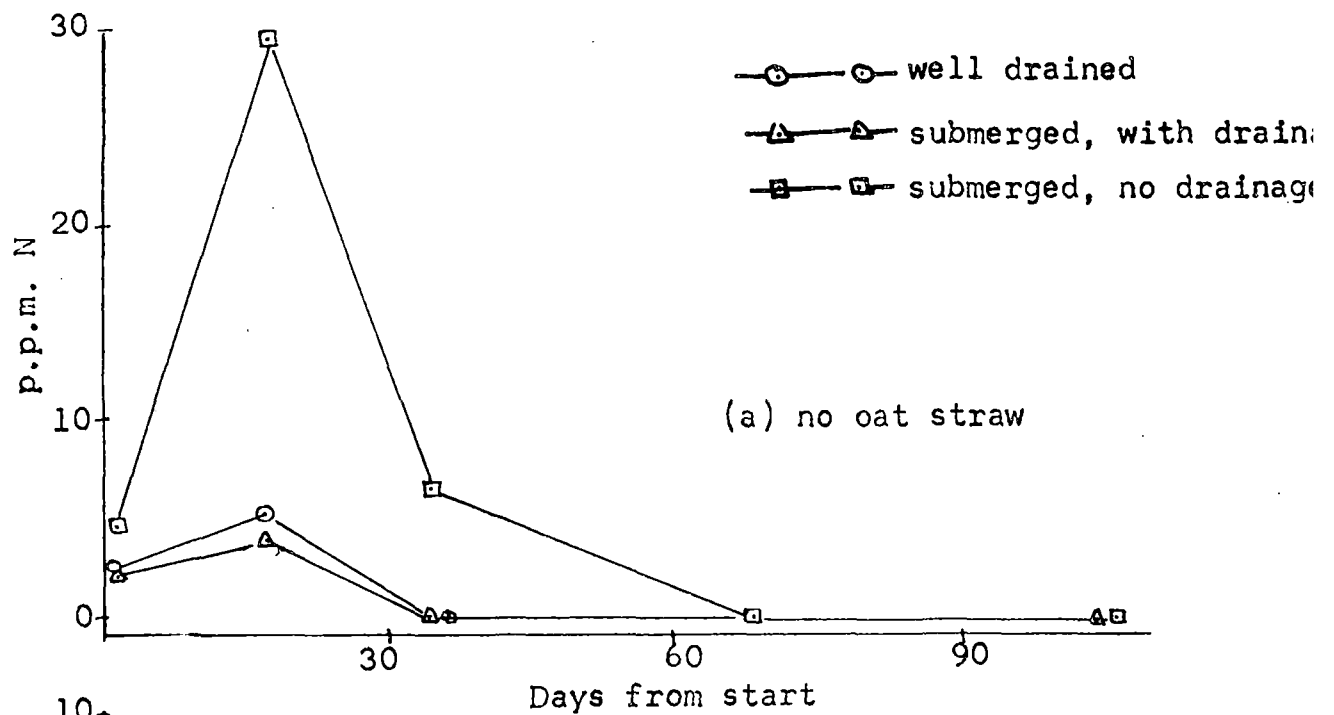


Fig. 13. Changes in nitrate N in percolates from pH 4.9 treatments.

matter content. The low content of iron is not entirely responsible for the low figure for oxidizable matter because iron accounts for only a fraction of the oxidizable matter. Apparently the presence of nitrate prevents the accumulation of the organic products of anaerobic metabolism.

Oxidizable matter as determined by oxidation of the sample with potassium permanganate under standard conditions, as mentioned earlier, is not an absolute measure of the concentration of reduced products. For this reason it cannot be used to characterize the degree of reduction of widely different soils. But for a given soil, this determination provides a simple and satisfactory index of the extent of reduction.

Nitrate. The results of the nitrate analysis are given in detail along with the other analytical data in Tables 1-5 of the Appendix. The mean values for each treatment are given likewise in Tables 9-16 of the Appendix.

The results reveal striking differences among the treatments. Differences are apparent not only in the course of nitrate changes but even in the initial concentrations of nitrate.

The initial nitrate concentrations varied widely as the following figures indicate:

"Treatment" pH	Nitrate N in p.p.m. in percolate
4.9	2.0 - 8.6
5.7	150 - 345
6.0	250 - 620

The high nitrate concentrations of the pH 5.7 and 6.0 soils is readily understood when it is recalled that an acid soil under sod was treated with lime, moistened, and left kept in a greenhouse for four weeks during a hot summer. The variability within a treatment may be attributed to the difficulty of obtaining a solution which had come into contact uniformly with the soil, by the method adopted for collecting the percolates.

The changes in nitrate concentration follow the expected course in the pH 5.7 and pH 6.0 treatments. Those for the pH 5.7 treatment are represented graphically in Fig. 14.

The graphs show that in all cases there is a progressive decrease in nitrate concentration. The rate of decrease is most marked in the submerged soils with drainage, intermediate in the well drained soils, and least in the submerged soils with no drainage. Oat straw has accentuated the disappearance of nitrate at all three levels of drainage but the effect is most marked in the submerged soils with no drainage.

The rapid disappearance of nitrate from the well drained soils and submerged soils with drainage is largely, if not entirely the result

of losses by leaching. The equally rapid loss of nitrate from the submerged no-drainage treatment with 0.4 percent oat straw is undoubtedly due to active denitrification. The remarkable feature, however, is that even under the anaerobic conditions that prevail in a submerged soil, nitrate may persist for an appreciable length of time provided excessive amounts of organic matter are not present.

The course of changes in nitrate concentration in two of the pH 4.9 treatments exhibit striking anomalies. This is clear from a glance at the graphs in Fig. 13.

The 0.2 percent oat straw treatments follow the usual course of decrease in nitrate concentration with time. But in the no-oat-straw treatment and the 0.4 percent oat straw treatment, the submerged soils with no drainage show a marked increase in nitrate in the first 17 days following submergence. The graphs, however, are deceptive because they associate this extraordinary behavior with entire treatments when in reality the anomaly stems from the peculiar behavior of one of the replicates in each of these two treatments. The first reaction was to dismiss the analyses as the result of accidental contamination during analysis. This could not be done in the face of not only a whole series of confirmatory chemical analyses but also differential plant responses. (V. treatments III and IX in Tables 2 and 17 of Appendix.) The figures clearly indicate that the increase in nitrate concentration is not spurious. This raises the question: how did nitrification proceed in the presumably anaerobic environment of a rather acid soil?

Nitrite. The results of the nitrite analyses confirm the observation of many investigators that nitrites do not accumulate in concentrations exceeding 3 p.p.m. N. The highest concentration observed in the submerged soils at any stage of the experiment was 2.6 p.p.m. N, despite the extraordinarily high initial nitrate concentrations. During the greater part of the growing season the nitrite concentration was of the order of 0.01 p.p.m. N in the soil solution for the majority of the submerged soils.

Ammonium. The ammonium concentrations in the soil solutions from each of the 81 pots on the several sampling dates are given in Tables 1-4 of the Appendix. The mean values for each of the 27 treatments are presented with those of the other analyses in Tables 9-13 of the Appendix. They are reproduced in Table 8 on page 99, for convenience.

The results show that the three treatment factors pH, oat straw level, and drainage have all influenced the course of changes in ammonium concentrations. These changes are easy to follow if the factors that influence the ammonium concentration in the soil solutions are borne in mind.

The concentration of ammonium in the soil solution of a submerged soil is governed by two factors: (i) the total ammonium content

of the soil; and (ii) the cation exchange equilibria in the soil. The total ammonium concentration at any time represents the balance between the initial ammonium content and ammonia released from organic matter on the one hand, and losses by leaching and assimilation by the plants on the other. An increase in concentration of other cations may cause an increase in the concentration of ammonium in solution by displacing ammonium from the exchange complex.

The influence of pH is most prominent at the first sampling. The pH 4.9 soils all have a soluble ammonium content which is almost double that of the pH 5.7 and 6.0 soils. This is due chiefly to lower absorption of ammonium by the unsaturated soil colloids at pH 4.9 than by the colloids with a higher proportion of calcium. The influence of pH in the later stages is difficult to identify owing to the confounding effect of differential growth of the rice plants.

The influence of organic matter on the changes in ammonium concentrations is most marked in the submerged no drainage treatments. There is a tendency for ammonium concentrations on a given sampling date to increase with the oat straw content. This effect is due principally to the retardation of growth of the rice plants perhaps by a high concentration of reduced products.

Of the three treatment factors, drainage has had the most pronounced effect. This is brought out clearly in Figures 15 and 16.

The well drained soils all have their ammonium concentration reduced to a very low value after 34 days from the start. The rate of decline is more rapid at the two higher pH levels than at pH 4.9, owing to nitrification. The submerged soils with drainage show a marked but slower decline than the well drained soils. This may be attributed to (i) the somewhat slower growth of the rice plants; and (ii) release of NH_4^+ from the soil colloids by Fe^{+2} and Mn^{+2} liberated by reduction. The submerged soils with no drainage exhibit a much slower decline and in the case of the pH 5.7 and 6.0 treatments a tendency even to rise during the first 34 days.

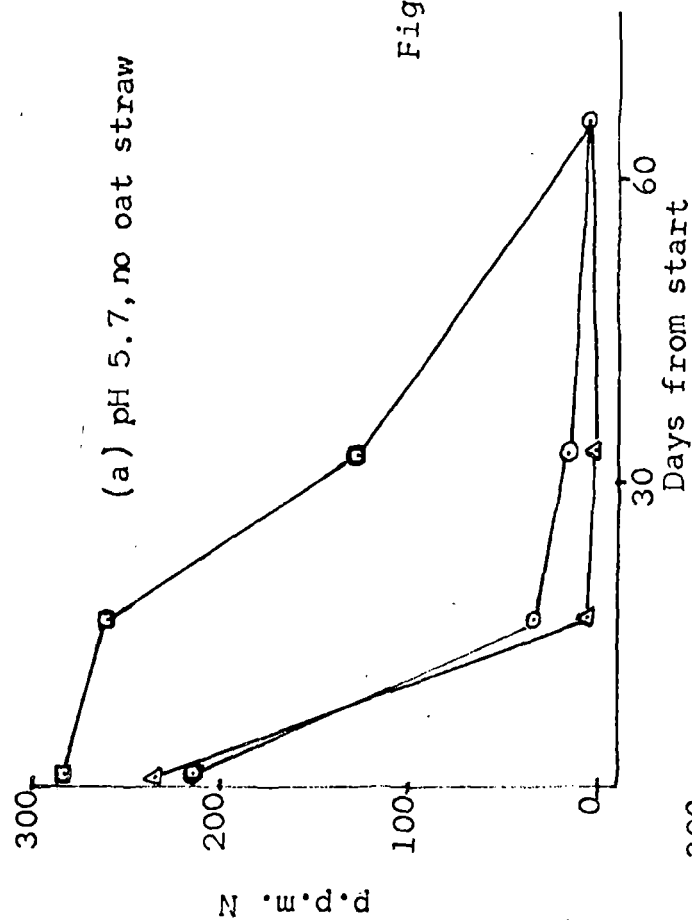
The slower decline of the undrained than the drained soils in the pH 4.9 treatments is no doubt due principally to the absence of leaching losses. The relatively high level of the ammonium concentrations in these treatments may be ascribed to (i) slower growth of the plants; and (ii) greater release of NH_4^+ from soil colloids by Fe^{+2} and Mn^{+2} than in all other treatments. The maintenance of the ammonium concentration at the original level for about three weeks in the pH 5.7 and 6.0, may be due to greater ammonification at these pH levels than at pH 4.9. The subsequent rapid decline may be laid to rapid assimilation by the rice plants.

The important conclusions from this study are: (i) appreciable amounts of ammonium may be lost in the drainage from a submerged soil; (ii) the presence of oat straw instead of immobilizing ammonium seems to increase the amount in solution in the submerged soils.

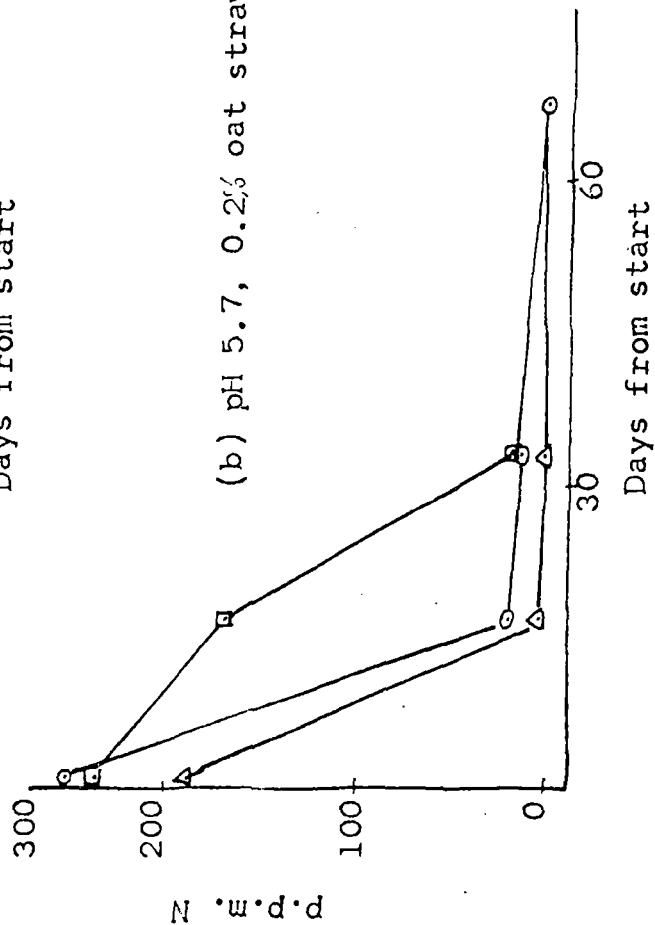
TABLE 8
CHANGES IN CONCENTRATION OF AMMONIUM
DURING THE PERIOD OF GROWTH

Treatment No.	Treatment			Ammonium N in p.p.m. in Percolates on Days from Start				
	pH	Oat Straw %	Drainage	1	17	34	67	108
I	4.9	0.0	w.d.	26.6	5.4	0.3	0.1	-
II	"	"	s.w.d.	27.3	9.1	3.0	0.6	0.9
III	"	"	s.n.d.	26.7	23.9	12.1	4.6	5.6
IV	4.9	0.2	w.d.	-	4.9	0.2	0.1	-
V	"	"	s.w.d.	27.4	8.9	5.0	0.6	0.9
VI	"	"	s.n.d.	27.3	19.1	14.3	3.8	5.8
VII	4.9	0.4	w.d.	26.6	4.5	0.1	0.1	-
VIII	"	"	s.w.d.	27.5	12.1	9.8	0.4	0.7
IX	"	"	s.n.d.	28.2	25.0	16.8	10.6	8.0
X	5.7	0.0	w.d.	14.5	1.0	0.6	0.3	-
XI	"	"	s.w.d.	19.0	7.8	4.6	0.2	0.4
XII	"	"	s.n.d.	16.1	16.8	7.9	4.5	4.4
XIII	5.7	0.2	w.d.	15.3	1.0	0.4	0.2	-
XIV	"	"	s.w.d.	15.8	9.9	3.5	0.1	0.4
XV	"	"	s.n.d.	16.0	15.7	16.2	4.3	4.7
XVI	5.7	0.4	w.d.	14.8	1.5	0.4	0.2	-
XVII	"	"	s.w.d.	13.2	12.8	6.5	0.2	0.3
XVIII	"	"	s.n.d.	15.8	18.1	21.6	3.6	6.0
XIX	6.0	0.0	w.d.	16.5	1.1	1.1	0.2	-
XX	"	"	s.w.d.	21.7	9.3	3.8	0.2	0.4
XXI	"	"	s.n.d.	18.7	18.0	7.4	4.8	5.0
XXII	6.0	0.2	w.d.	14.6	1.1	0.5	0.2	-
XXIII	"	"	s.w.d.	15.7	10.6	4.9	0.2	0.4
XXIV	"	"	s.n.d.	13.4	15.6	13.8	3.9	4.1
XXV	6.0	0.4	w.d.	-	1.1	0.5	0.2	-
XXVI	"	"	s.w.d.	15.4	11.5	5.3	0.2	0.2
XXVII	"	"	s.n.d.	17.2	22.2	14.2	2.7	4.0

(a) pH 5.7, no oat straw



(b) pH 5.7, 0.2% oat straw



(c) pH 5.7, 0.4% oat straw

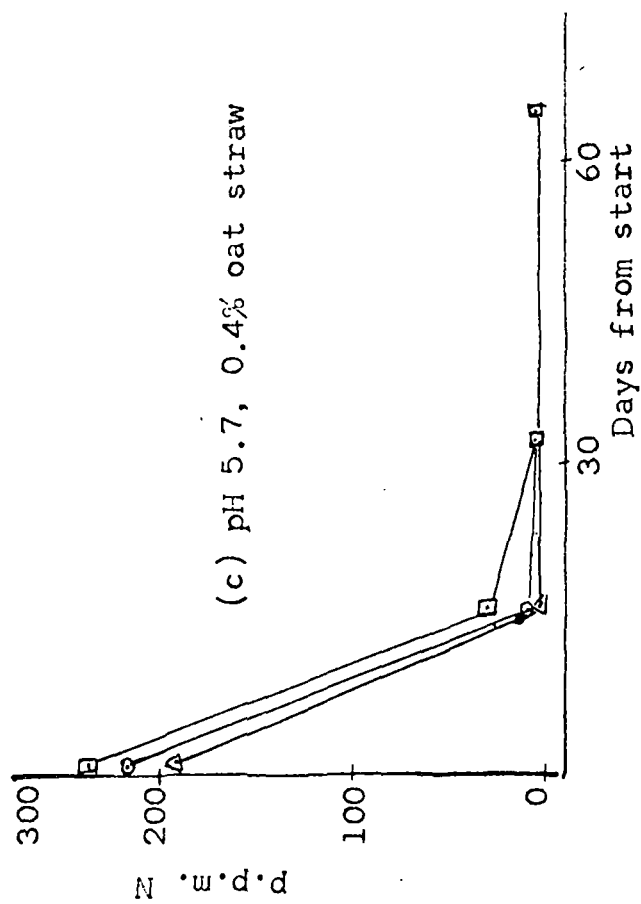
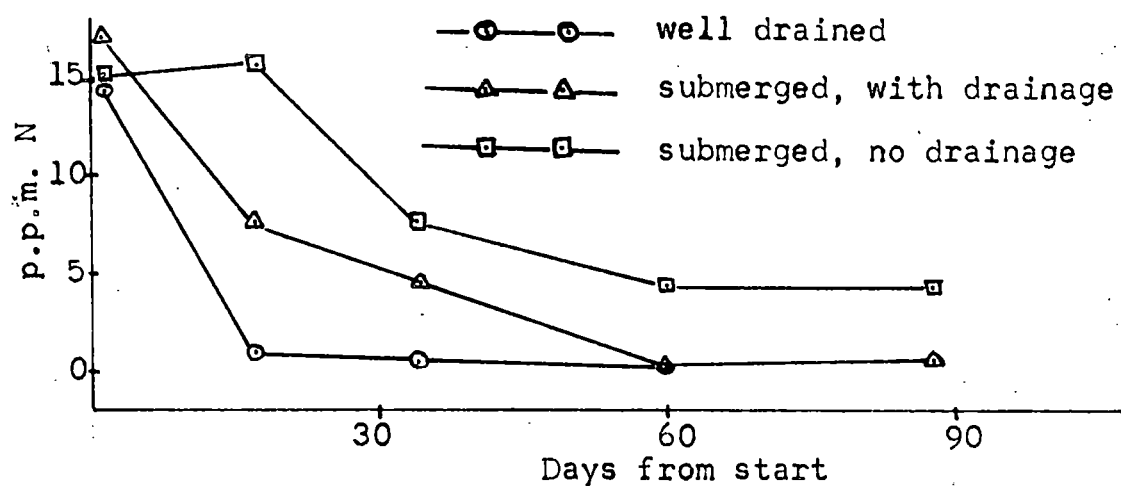
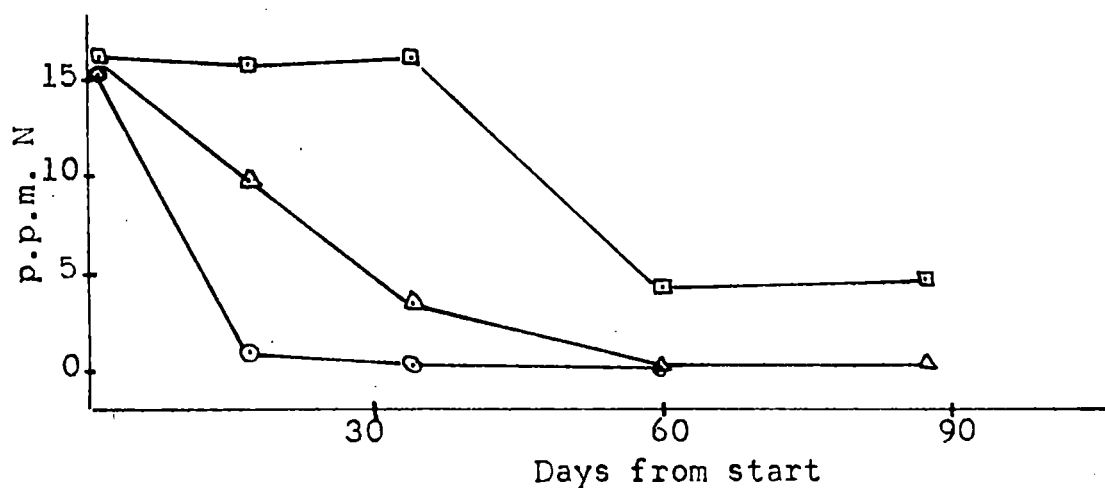


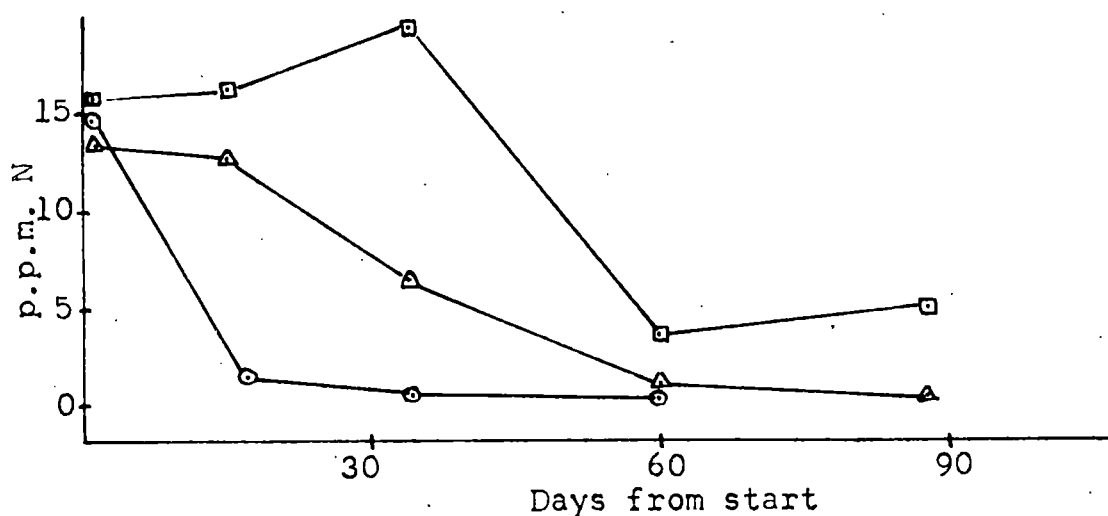
Fig. 14. Changes in concentration of Nitrate nitrogen in percolates from pH 5.7 treatments.



(a) No oat straw

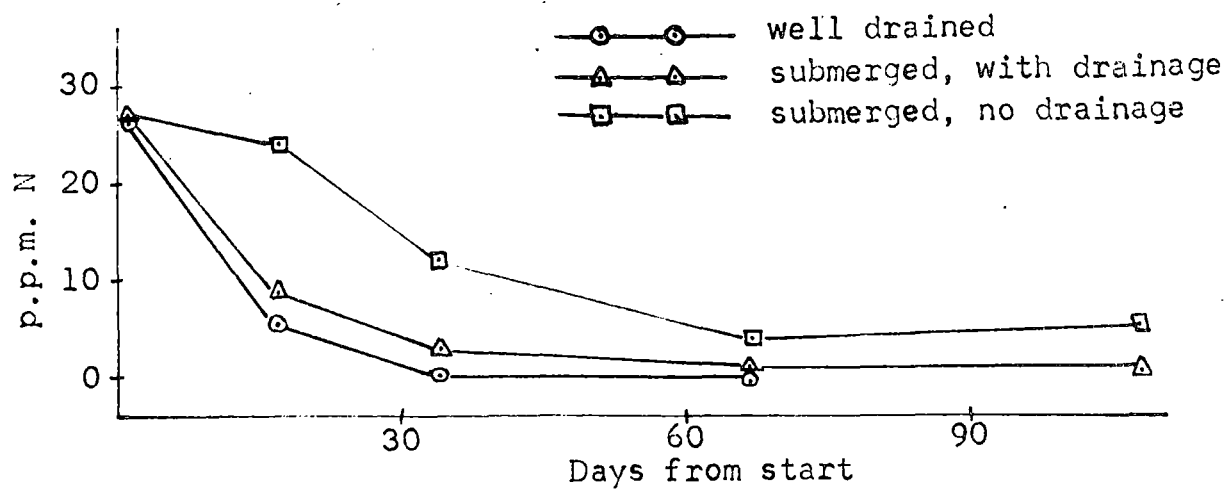


(b) 0.2% oat straw

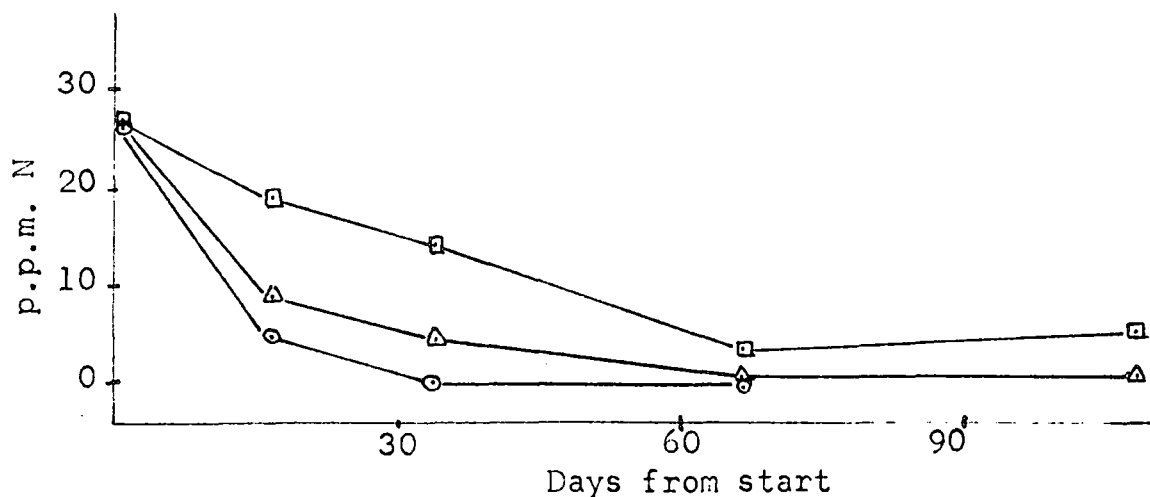


(c) 0.4% oat straw

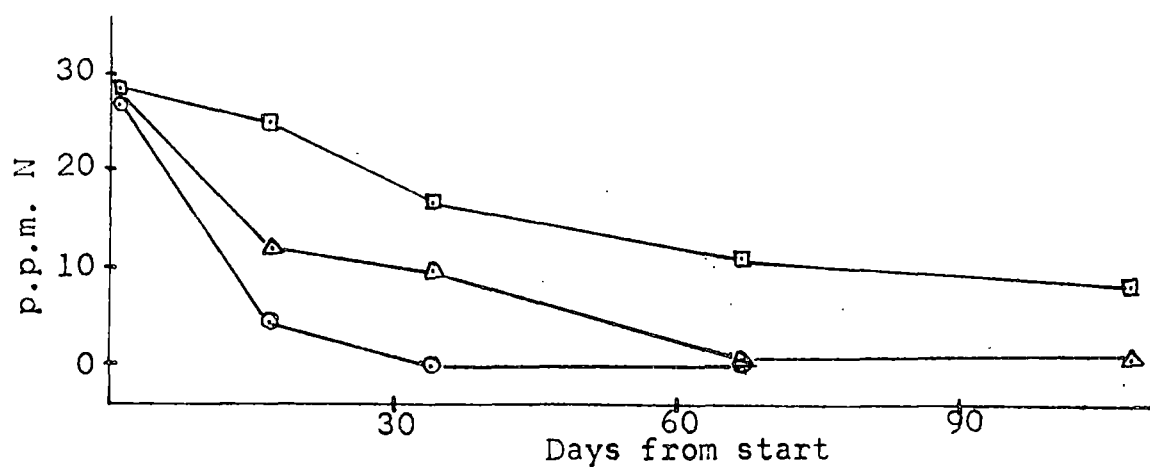
Fig. 16. Changes in concentration of NH_4^+ in percolates from pH 5.7 treatments during period of growth.



(a) No oat straw



(b) 0.2% oat straw,



(c) 0.4% oat straw

Fig. 15. Changes in concentration of NH_4^+ in percolates from pH 4.9 treatments during the period of growth.

4.322 Analyses of Soil Samples

Although the changes in composition of the percolates from the submerged soils are probably of greater ecological significance than those of the soils themselves, the chemical analyses of the percolates do not give a complete picture of the extent of the reduction process in these soils. For this reason the changes in concentration of reduced substances in acid extracts of the soil were determined.

Unfortunately, the chemical analyses of 81 soil samples for the several constituents examined separately in 0.1 N H_2SO_4 and Morgan extracts, several times during the growing season, called for the expenditure of time and effort that necessitated sacrifice of accuracy for the sake of speed and expediency. Despite this limitation the analyses of the soil samples are generally in agreement with those of the soil solutions and also confirm many points predicted by theory.

(a) 0.1 $\text{N}_2\text{H}_2\text{SO}_4$ extracts

Ferrous iron. The iron in the extracts was determined by the o-phenanthroline method without a preliminary reduction with hydroxylamine. The analyses are therefore taken to represent the ferrous iron content of the soils although some ferric iron may have been reduced by organic matter during the extraction procedure. The results of this determination are given in detail in Tables 6-8 while the mean values for each treatment are presented in Tables 14-16 of the Appendix.

As the analyses of the percolates revealed, the well drained soils constitute a class by themselves for they are all characterized by a low content of reduced iron during the entire season. The behavior of the submerged soils is somewhat different. In the early stages the ferrous iron contents of the submerged soils with drainage are higher than in the corresponding soils with no drainage. The analyses of the percolates indicated a similar relationship in the early stages. In the final stages the ferrous iron contents of the submerged soils with and without drainage do not differ markedly, though the percolates showed wide differences. This suggests that reduction of iron has proceeded to practically the same extent under both conditions of drainage. The slightly lower figures for the ferrous iron content of the soils with drainage may be attributed to drainage losses.

The effects of pH and organic matter on the ferrous iron content of the soils are discernible but are not as pronounced as they were with the percolates. Despite the marked difference in the concentration of iron in the percolates from the no-drainage soils of the pH 4.9 treatment and the two higher pH treatments at the final sampling, the ferrous iron contents of the soils is practically the same. This suggests once again that reduction has proceeded to nearly the same extent at all pH levels.

The organic matter level has influenced the rate of reduction of iron but has not apparently affected the extent of reduction.

An interesting question is the proportion of soluble to insoluble ferrous iron in the submerged soils. Naturally, this ratio varies widely with pH, drainage level and organic matter content. Calculations show that even under the conditions most favorable to the solution of ferrous iron, only about 5 percent of the reduced iron is in solution. The rest is present in the solid phase probably as exchangeable Fe^{+2} , $\text{Fe}(\text{OH})_2$, FeCO_3 and FeS .

Oxidizable Matter. This includes ferrous iron, sulfides and easily oxidizable organic compounds of unknown identity. The analyses are given in Tables 6-9 and 14-16 of the Appendix.

The results indicate a difference between the submerged soils and the well drained soils. Differences due to pH, oat straw level, and presence or absence of drainage are neither marked nor consistent. Comparison of the figures for oxidizable matter with the corresponding ones for ferrous iron shows that iron accounts for only an insignificant fraction of the permanganate consumed. The absence of the expected marked contrast between the well drained and the submerged soils suggests that fresh organic matter, principally rice roots present in the samples, was largely responsible for the reduction of the permanganate solution used in these determinations.

(b) Morgan Extracts

The objectives of the tests with extracts of the soils in Morgan's reagent were: (i) to determine the extent to which the availability of plant nutrients was affected by the reduction of soil; and (ii) to investigate the possibility of characterizing the extent of reduction of a soil in the course of routine soil tests with submerged soils. Unfortunately, time did not permit the determination of all the constituents planned so that figures are available only for iron and manganese on three sampling dates and for phosphorus, on one sampling date. The detailed analyses are given in Tables 6-9 and the mean values for each treatment in Tables 14-16 of the Appendix.

Iron. The changes in concentration of iron extractable with Morgan's reagent tends to follow the pattern of the percolates, in the early stages, and the sulfuric acid extracts, in the final stages.

The well drained soils are all characterized by a relatively low iron concentration which varies little with time and treatments. Some pH and organic matter treatment trends are, however, perceptible: the iron extractable in Morgan's solution tends to decrease with increase in pH and increase with rise in oat straw level.

In the submerged soils iron in Morgan extracts follow exactly the same pattern as iron in the percolates, during the early stages. It is higher in the drained soils than in the undrained soils at pH 5.7

and 6.0, and vice versa at pH 4.9. Seventy days after submergence the two drainage treatments, regardless of pH and organic matter levels, tend towards a common level for iron soluble in Morgan's reagent.

The results suggest: (i) that the final amount of reduced iron in the submerged soils is not markedly affected by pH and oat-straw levels although the concentration of iron in the percolates is; (ii) that the concentration of iron extractable with Morgan's reagent gives a fair indication of the extent of reduction of a soil, in the early stages of submergence.

Manganese. The changes in concentration of manganese extractable with Morgan's reagent run a course that is roughly parallel to those of iron, for the submerged soils. The actual concentrations of manganese are, however, considerably lower than those of iron. As in the case of the percolates the Fe:Mn ratio widens as reduction proceeds. At the third sampling the Fe:Mn ratio is of the order of 20 for the Morgan extracts compared with approximately 7 for the percolates at the same sampling. The manganese concentrations at the third sampling in the submerged soils with drainage are uniformly lower than those of the corresponding no drainage treatments, suggesting a loss of manganese in the drainage.

The behavior of the well drained soils is different. The oat-straw level, rather than pH, seems to determine the level of manganese extractable in Morgan's reagent. This is in harmony with the principles of manganese reduction discussed in an earlier section.

Phosphorus. The single series of phosphorus analyses are given in Table 8 of Appendix. They confirm the theoretical predictions and the practical observations of several investigators (14, 75, 153, 166, 254) that the solubility of phosphate both in the soil solution and acid extractants increases on submergence and reduction of a soil.

4.33 Growth and Yield of Rice

4.331 Growth Characteristics

The eight-week-old rice seedlings which were about 60 cm. in height were topped at a height of 45 cm. and transplanted, six plants to a pot, on August 1, 1953. The plants took on well and replacements were few.

Two weeks lapsed before treatment differences became evident. The most striking differences at this time were observed among the drainage treatments. Contrary to expectation, the well drained treatments were distinctly superior to the submerged treatments. Between the two submerged treatments, those with drainage were uniformly superior to the treatments without drainage, the difference being most marked in the pH 4.9 treatments.

These differences became intensified as the season progressed and at the end of the fourth week the well drained treatments without exception stood out distinctly above the rest, especially in height. By this time differences between the two submerged treatments also had become exaggerated. The submerged treatments with drainage looked distinctly better than those without drainage. The only exception to this behavior was in the pH 5.7 treatment: the no-oat-straw, submerged no-drainage treatment was distinctly superior to the submerged with drainage treatment.

Differences among the pH and organic matter treatments were also apparent at this stage. Among the well drained treatments, growth was best at pH 4.9 and poorest at pH 5.7. Strangely enough, among the submerged treatments with drainage neither pH level nor oat straw level seemed to have had any appreciable influence. In the submerged treatments with no drainage, however, there were unmistakable responses to pH and oat-straw levels. For a given oat-straw treatment there was an improvement in growth with increase in pH level while for a given pH treatment there was a marked decline with increase in organic matter level.

It may also be noted that up to this stage variability among replicates of the same treatment was least in the well drained soils, intermediate in the submerged soils with drainage and most in the submerged soils with no drainage. It will be recalled that a similar trend was noticeable in the chemical analyses in the early stages.

By the end of the fourth week after transplanting the tillering phase was practically over and marked responses of tillering to treatments were apparent. The responses were both qualitative and quantitative. The well drained treatments produced thin, tall tillers compressed together at the base. The number of tillers in the pH 4.9 in general was high but it decreased markedly with increase in pH level. The oat-straw treatments had little influence on tillering in the well drained soils except at the highest levels and that only in the pH 4.9 and 5.7 treatments. In the submerged soils, the tillers were squat, succulent and spread out fanwise. Tillering was profuse in the submerged soils with drainage regardless of pH and oat straw levels. Tillering was equally good in the no-oat-straw, submerged, no-drainage treatments at pH 5.7 and 6.0 but in the other submerged, no-drainage treatments tillering was markedly affected by pH and oat straw levels. For a given pH treatment tillering decreased markedly with increase in oat straw level while for a definite oat straw level tillering increased markedly with increase in pH level.

The next four weeks were marked by a comparative lull in activity in all treatments, especially in the well drained treatments. The well drained treatments appeared to languish while the submerged treatments continued to grow, though at a slower rate than before. As a result of this differential growth the gap between the well drained treatments and submerged treatments was considerably narrowed by the end of this period. But other differences appeared.

Up to the beginning of the fifth week from transplanting the plants were all healthy green in color and upright in growth. During the four weeks that followed, however, the plants in the submerged treatments with drainage, and the no-oat-straw, submerged, no-drainage treatments of pH 5.7 and 6.0 assumed a chlorotic appearance, which was most marked in the older leaves. Similar symptoms in a more acute form were observed in the well drained, 0.2 percent and 0.4 percent oat-straw treatments at pH 4.9. This chlorosis was probably associated with a low nitrogen supply due to leaching and assimilation in the submerged, drainage treatments and immobilization in the well drained treatments.

There were differences also in the growth habit of the plants. The submerged treatments were all erect and upright. So were the well drained treatments at pH 4.9. In marked contrast to these were the well drained soils of the pH 5.7 and 6.0 treatments. The plants of these treatments had apparently ceased to grow and the laminae, though green and apparently healthy, lacked strength and hung loosely, giving the plants a drooping appearance.

More important by far than the contrast in growth habit between the well drained treatments and the submerged treatments are certain symptoms that were observed in some of the submerged treatments. Although the significance of these symptoms was not at all realized then, sufficiently accurate notes were made at the time the symptoms were observed to bring out the strong resemblance of these symptoms to those of a physiological disease of rice about which detailed information became available only long after the experiment.

About six weeks after transplanting brown spots were observed on the older leaves of some of the submerged treatments. The spots were most prominent in the pH 4.9, 0.4 percent oat-straw, submerged, no-drainage treatment. Within this treatment replicate 2 (pot no. 26), the poorest looking of the three replicates showed them to a greater degree than the other two. The brown spots were also noted in the pH 4.9, 0.2 percent oat-straw, submerged no-drainage and to a lesser extent in the no-oat-straw, submerged, no-drainage treatment of the same pH level.

The next symptom to be noted was a reddish discoloration of the tip of the affected leaves. This was first observed in the 0.4 percent oat-straw and subsequently in the 0.2 percent oat-straw and even in the no-oat-straw treatment. As the disease progressed the reddish discoloration spread along the edges towards the base of the leaves. The affected portions dried up while the rest of the leaves remained green, though speckled. The situation 65 days after transplanting was as follows: speckling of leaves and pronounced marginal scorch of older leaves in the 0.4 oat-straw treatment, with pot no. 26 showing the most severe symptoms; speckling of leaves and reddish color along the leaf margins but only the leaf tips scorched, in the 0.2 percent oat-straw treatment; and less pronounced speckling and tip burn in the no-oat-straw treatment. The subsequent course of the disease will be described after an account of the next phase in the growth of the rice plants -- the reproductive phase.

The ninth week after transplanting marked the beginning of a burst of activity by the plants of the majority of the submerged treatments and the oat-straw treated, well drained soils of the pH 4.9 treatment. The plants of the oat-straw treated, well drained, pH 4.9 treatment regained some of their green color, elongated slightly, and headed. But the plants of submerged soils with drainage, on the whole, and all except the diseased submerged, no-drainage treatments acquired a deeper green color, underwent a rapid elongation and headed shortly after. Emergence of inflorescence in these treatments was spread over a period of about five days, commencing October 6, i.e., 67 days from transplanting. The elongation of culms continued for a further two weeks. At the end of this period the plants of these treatments were towering above those of the well drained treatments, behind which they had earlier lagged so much. These changes are brought out dramatically in Figures 17-22, for some of the treatments. While the plants of these treatments were forging ahead those of the well drained treatments continued to languish and along with plants of the high-oat-straw submerged no-drainage treatments, headed about a week after the other plants.

There were marked differences in the appearance of the panicles. All the submerged treatments, with the exception of the 0.4 percent oat-straw, pH 4.9 treatment, produced normal panicles whose florets appeared to undergo normal anthesis. The behavior of the plants of the well drained treatments presented a sharp contrast. The boot leaves were crinkled and etiolated in parts and the inflorescences emerged slowly and with difficulty. Besides, the culm at this stage underwent no elongation except in the 0.4 percent oat-straw, pH 4.9 treatment as Figures 17-22 indicate. The heads were thin and narrow and had a high proportion of florets which had soft, white lemmas and paleas and had apparently aborted. The plants of the pH 4.9 well drained treatments were a notable exception. Although heading was delayed and there was no elongation at time of heading, the panicles, though small, appeared to be normal and the florets appeared to undergo normal anthesis. The panicles of the plants of the 0.4 percent oat-straw, submerged no-drainage, pH 4.9 treatment were equally poor in appearance and also had a high proportion of aborted flowers.

Although the plants of the submerged treatments, with the single exception of the 0.4 percent oat-straw, no-drainage, pH 4.9 treatment, produced normal panicles with florets that opened normally it was noted later that a high proportion of the florets did not set into grain. The proportion of sterile florets varied widely and appeared to follow no treatment trends. Perhaps low temperature, coupled with light of low intensity and short duration, at heading time (October 6-12) was responsible for the high sterility. Nagato (160) reports that these two factors are a common cause of sterility in rice.

By the end of the heading and elongation phase, the differences among the treatments, which were observed earlier, were manifested in an accentuated form.

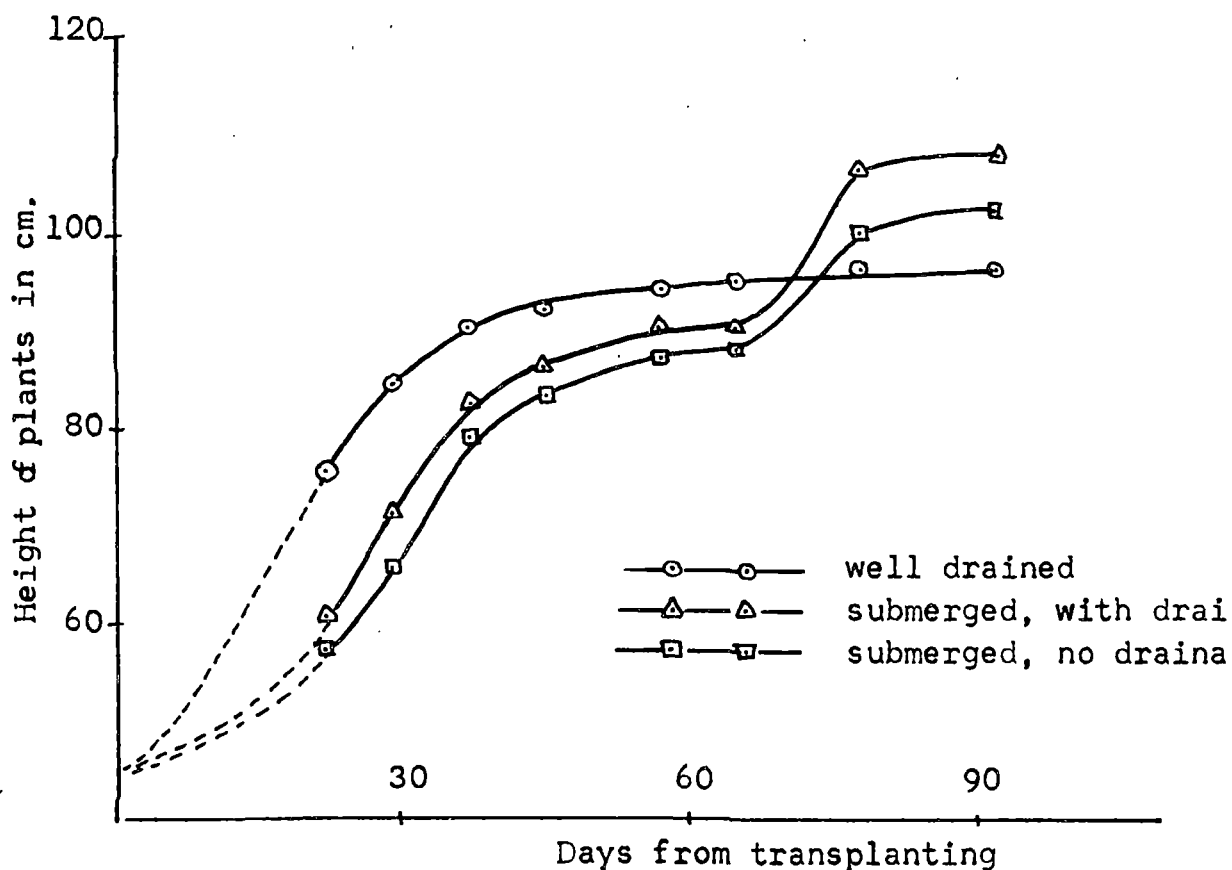


Fig. 17. Growth of rice plants: pH 4.9, no oat straw

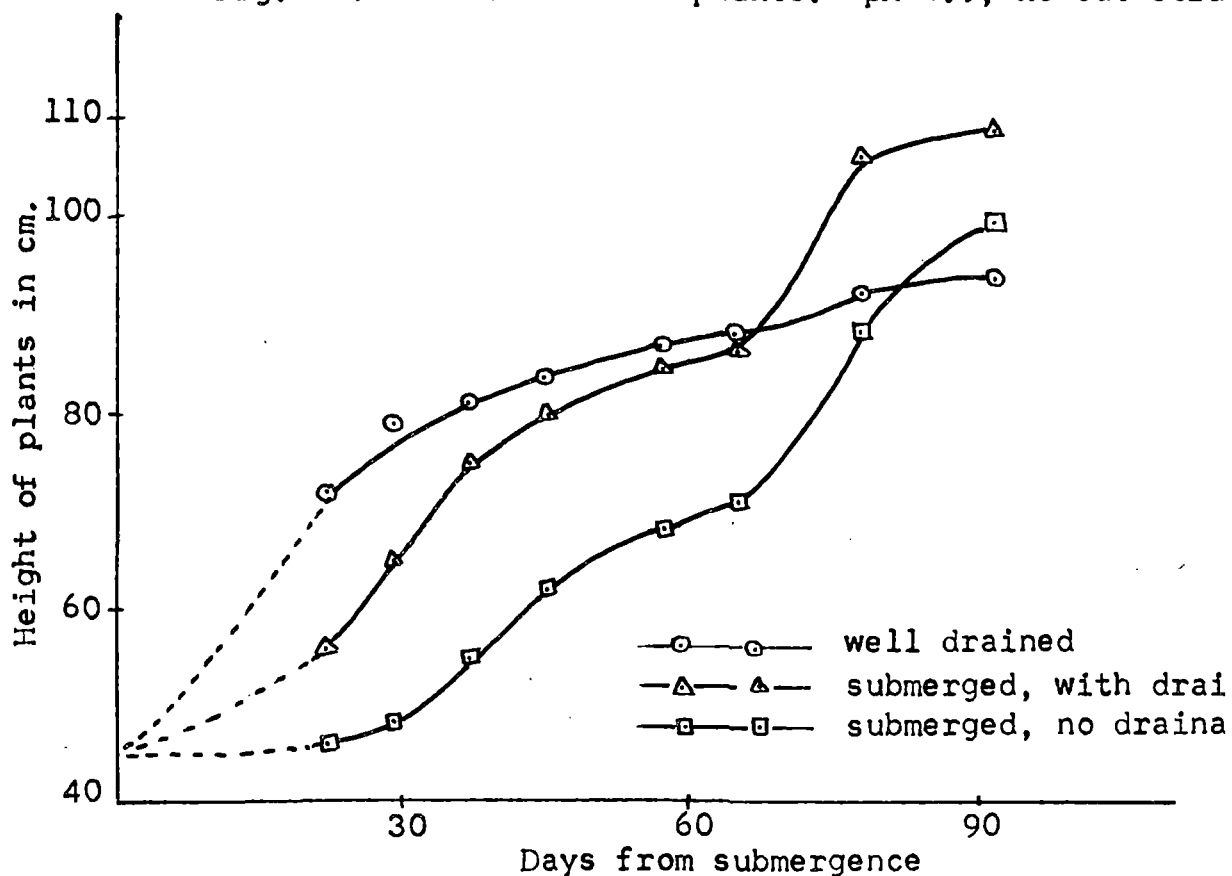


Fig. 18. Growth of rice plants: pH 4.9, 0.4% oat straw.

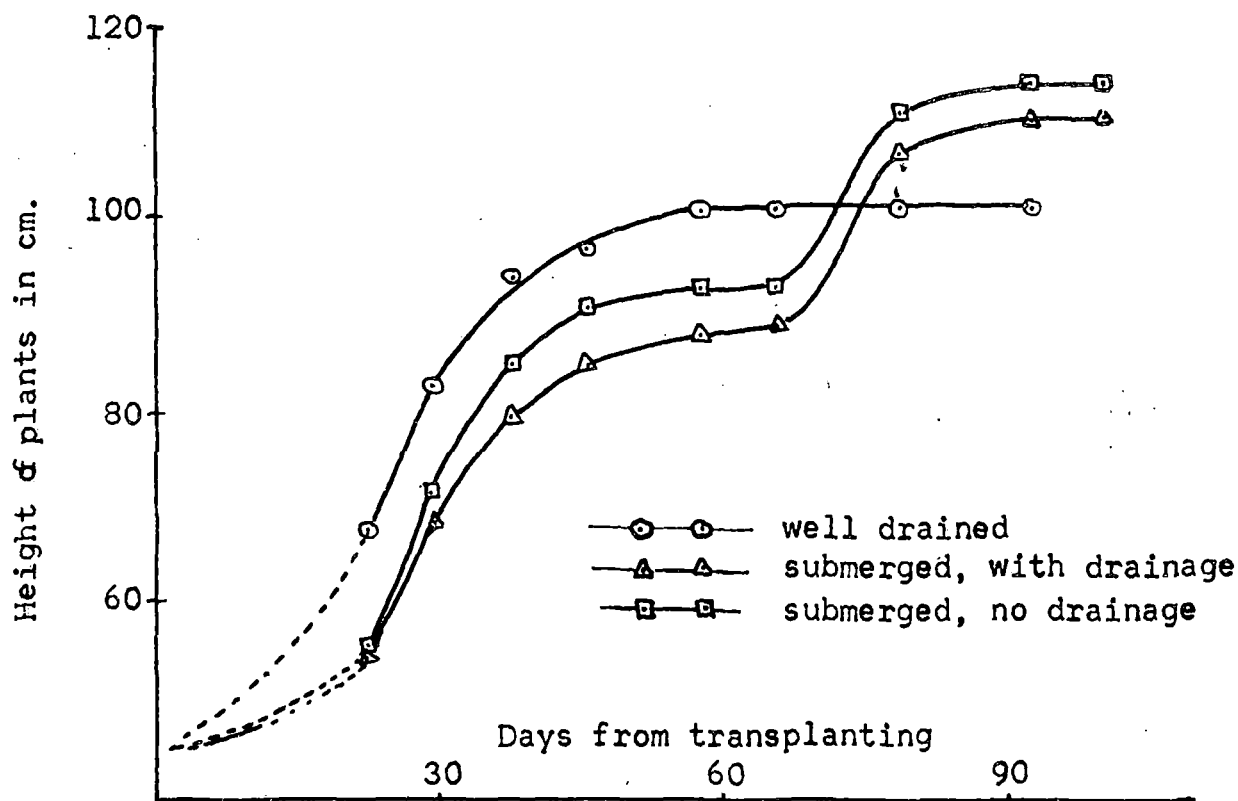


Fig. 19. Growth of rice plants: pH 5.7, no oat straw treatment.

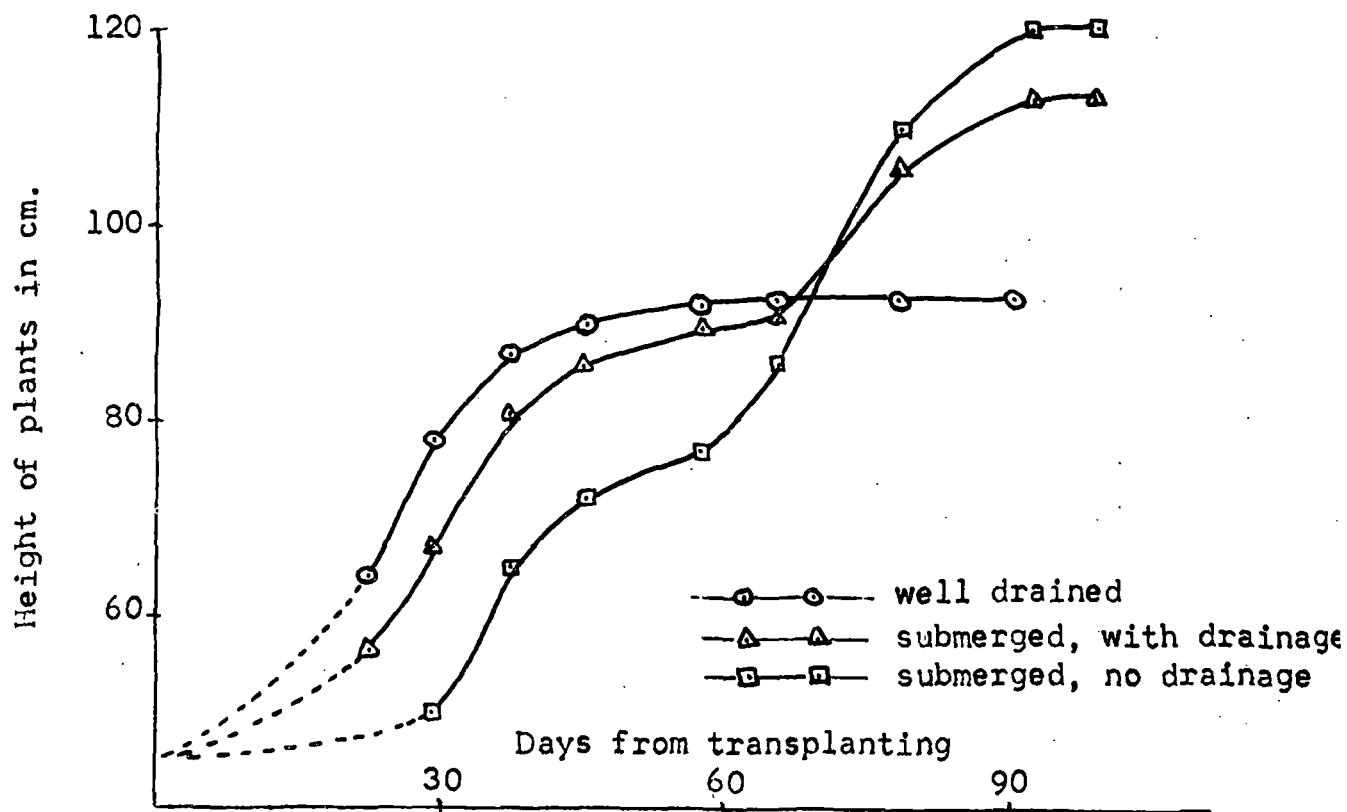


Fig. 20. Growth of rice plants: pH 5.7, 0.4% oat straw treatment.

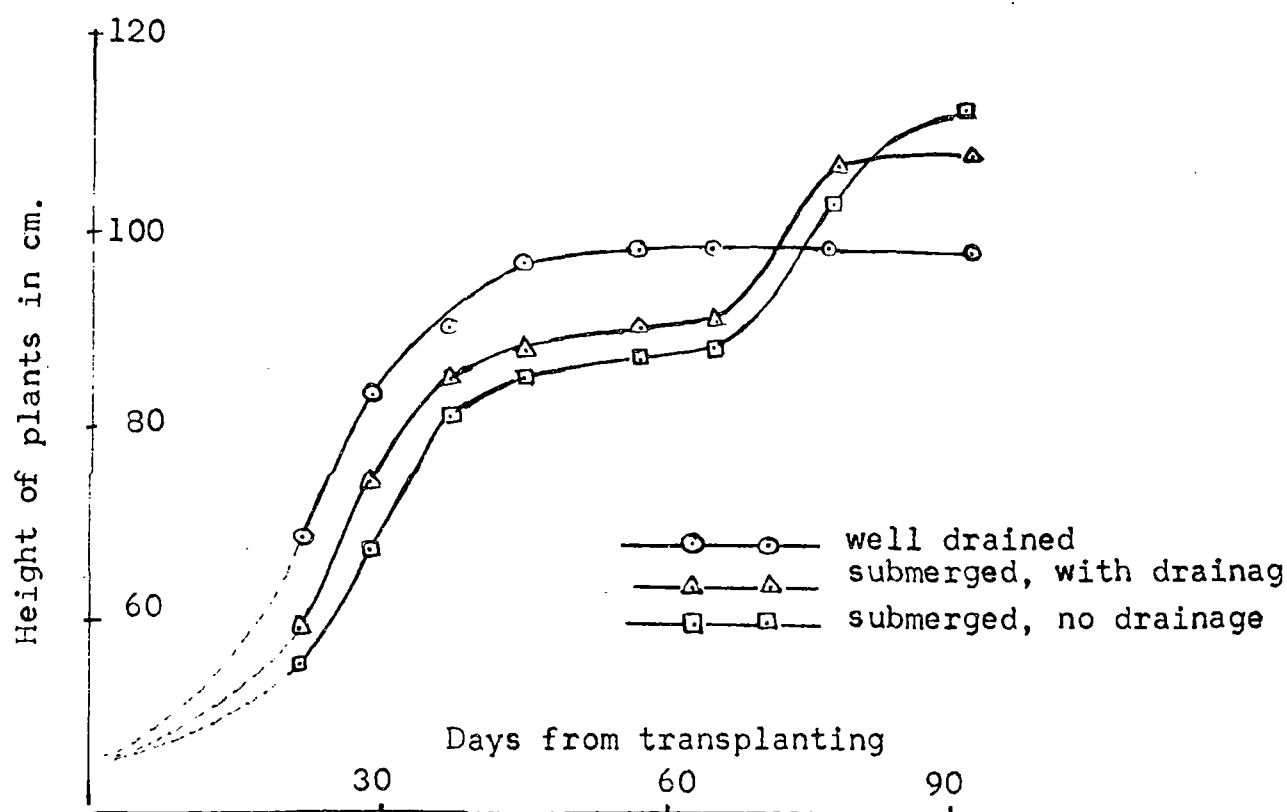


Fig. 21. Growth of rice plants: pH 6.0, no oat straw treatment.

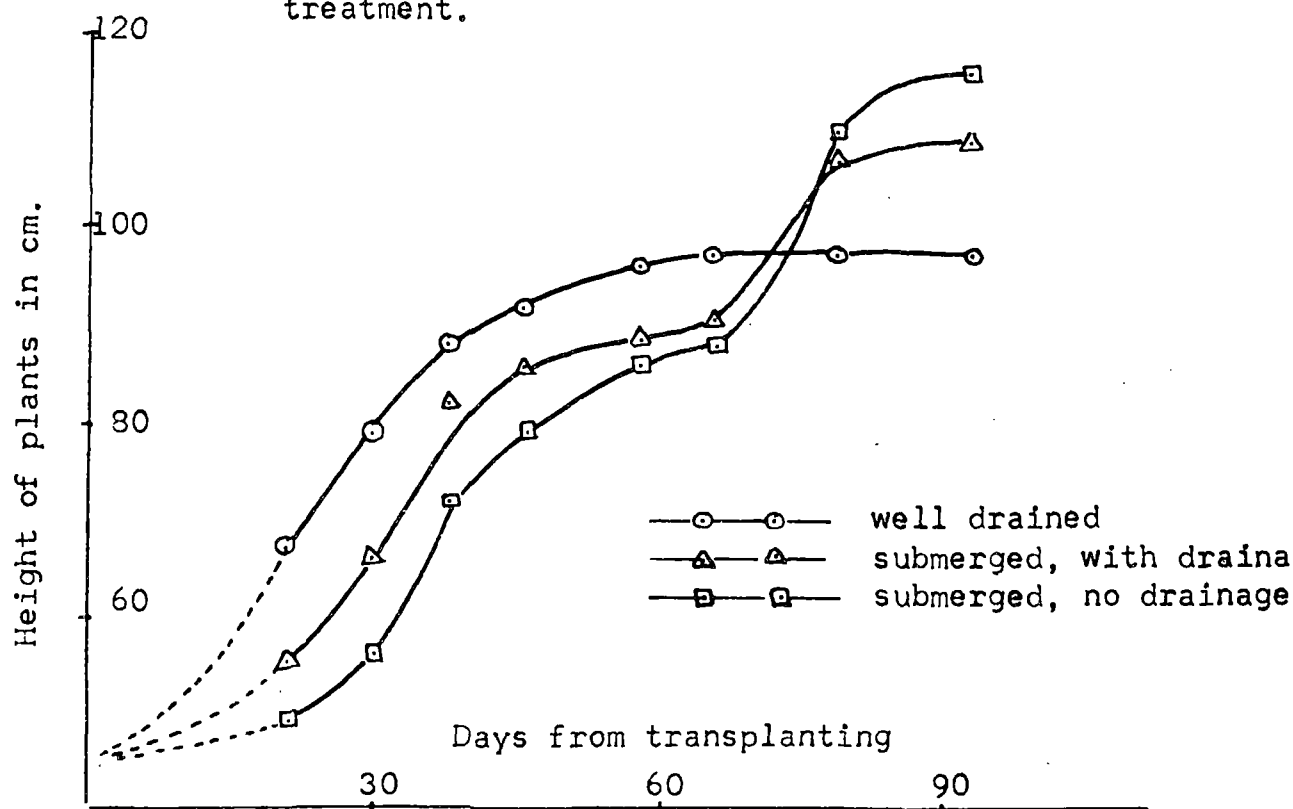


Fig. 22. Growth of rice plants: pH 6.0, 0.4% oat straw.

The well drained treatments, with the exception of those at pH 4.9 appeared stunted and poor with long drooping leaves. The majority of the submerged, with drainage treatments, regardless of pH and oat-straw levels, appeared normal, although they were somewhat paler green in color than the submerged, no-drainage treatments. Among the submerged no-drainage treatments, the most striking feature was the scorched appearance of the pH 4.9 treatment.

Reference has already been made to the brown spots, reddish discoloration and marginal scorch observed on the plants of these treatments. These symptoms had in the few intervening weeks become so severe that the diseased pots stood out prominently among the 81 pots, by their scorched appearance. The necrosis which at the earlier stage was confined to the margins of the older leaves had by this time affected the entire leaves, while the brown spots and reddish discoloration were now noticeable even in the younger leaves. The affected leaves had curled inwards, dried up and assumed a darker brown color than the dead leaves of the unaffected plants. Though the scorched appearance was common to all three submerged, no-drainage treatments it was most prominent in the no-oat-straw treatment, particularly in pots no. 7 and 9, simply because of the greater mass of leaves. In the 0.4 percent oat-straw treatment the scorching was severe and the brown spots and reddish discoloration of the tips of the young leaves was more marked than in the no-oat-straw treatment. But the plants were so spindly and so poorly furnished and the proportion of dead leaves which had broken loose and fallen into the pots so great that these pots did not have the same withered appearance as pots no. 7 and 9. Other striking features of the 0.4 percent oat-straw treatment were the unusually long internodes, the broad, green, horizontal laminae of the leaves, and the thin narrow panicles with an unusually high proportion of sterile florets. The plants of the 0.2 percent oat-straw treatment were in general intermediate in appearance.

So far the emphasis has been on the disease symptoms of the submerged, no-drainage treatments at pH 4.9. It is of interest to note that in the final stages some of these symptoms were observed in a milder form in the submerged with drainage treatments, also, at pH 4.9. There was also a suggestion of similar symptoms in the 0.4 percent oat-straw, no-drainage treatment at pH 5.7.

The observations on the growth of the rice plants may now be summarized and discussed.

The well drained treatments, at the start, were markedly superior to the submerged treatments at all pH and organic matter levels. This lead was maintained till about the time of heading when most of the submerged treatments made a dramatic recovery and surpassed the well drained treatments which made no further progress. Apparently an aerobic environment is a better milieu for the newly transplanted rice seedling than the anaerobic medium of a submerged soil. The slower growth of the plants in the submerged soils may be due to (i) deficiency of oxygen; (ii) excess of carbon dioxide; and, (iii) presence of reduced products.

The deficiency of oxygen may be a factor in the early stages when the air chambers of the roots are not fully developed. An insufficiency of oxygen would retard growth because of reduced accumulation of nutrients from the soil. An excess of carbon dioxide, like a deficiency of oxygen, retards the accumulation of nutrients and water. Since carbon dioxide in injurious concentrations may be present in the early stages of submergence the slower growth of the plants in the submerged soils may well be due to carbon dioxide toxicity. The presence of reduced substances, like Fe^{+2} and Mn^{+2} , in excessive amounts may be injurious to rice roots before they have developed a defensive mechanism of maintaining an oxidized environment in the immediate vicinity.

The better growth of transplanted rice in an aerobic environment, in the early stages, raises the question of the availability of iron. Possibly, the decomposition of roots damaged during transplanting render iron available (i) by keeping the redox potential in the immediate surroundings of the base of the plant, low (ii) by supplying substances that form chelates with iron and render it soluble. With the disappearance of this readily decomposable source of organic matter, iron is probably rendered unavailable, or the iron demands of the rice plant become greater in the later stages. The stagnation of plants in the later stages may be ascribed to reduced availability of iron. It is interesting to note in this case that, among the well drained soils, growth over the entire season was best at the lowest pH level, namely, 4.9.

Among the submerged soil treatments, those with drainage were better than those without at pH 4.9 and worse at pH 5.7 and 6.0. Further, among the submerged treatments with drainage there were no appreciable differences. It will be recalled that the chemical analyses were practically the same for all submerged, drainage treatments, irrespective of pH and organic matter levels.

In the case of the submerged soils without drainage, growth improved as the pH increased and the level of oat straw decreased. A similar parallelism was observed between the concentration of reduced products (Fe^{+2} , Mn^{+2}) and these treatment factors.

In regard to the symptoms, brown spots, reddish discoloration, and leaf scorch it is interesting to note that these were observed only in the submerged, no-drainage treatments of pH 4.9 -- all treatments which had a high concentration of reduced iron and manganese during greater part of the growing season.

Finally, it may be mentioned that within a given submerged treatment the largest number of tillers and the best growth was associated with the replicate in which nitrate was high and iron and manganese low at least in the early stages of submergence. (Compare pots no. 5, 8, 25, 35 and 45 in Tables 2 and 3, and in Table 17 of Appendix.)

4.332 Yield Data

Full details of the yields of straw, grain and roots for each of the 81 pots are given in Table 17 of Appendix. The mean values for each treatment are presented in Table 18 of Appendix. These figures confirm the treatment trends which were reported and discussed in a qualitative manner in the preceding section. The statistical analysis which will be made presently enables the assessment of these trends with greater precision.

(a) Straw Yields

The analysis of variance of the straw yields is given in Table 9. It is clear at once that all three treatment factors and their interactions have had a highly significant* effect on the yield of straw.

Of the main and interaction effects, drainage seems to be the factor responsible for the bulk of the differences among the treatments. On apportioning the drainage level sums of squares to its sources a further fact emerges: the bulk of the differences due to the drainage treatments lies between the well drained treatment on the one hand and the two submerged treatments on the other.

<u>Partition of Drainage Level Sums of Squares</u>			
<u>Source</u>	<u>Degrees of Freedom</u>	<u>Sum of Squares</u>	<u>Mean Square</u>
Drainage levels	2	5794.10	
Well drained vs. Submerged	1		5431.14**
Submerged, with drainage vs. Submerged, no drainage	1		362.96**

This analysis shows not only that the well drained treatments are highly significantly different from the submerged treatments as a class but that the submerged with drainage treatments are highly significantly different from the submerged, no-drainage treatments. The yield figures disclose the nature and magnitude of these differences.

<u>Drainage level</u>	<u>Straw Yield from 27 Pots (gm.)</u>
Well drained	969
Submerged, with drainage	1508
Submerged, no drainage	1368

Thus on the whole, the submerged with drainage treatment is the best; the submerged, no-drainage treatment is slightly (though highly significantly) inferior to it; and the well drained treatment by far the worst.

* High significance = significance at one percent level.

TABLE 9
ANALYSIS OF VARIANCE OF STRAW YIELDS

Source	Degrees of Freedom	Sum of Squares	Mean Square
Rows	8	757.28	
Columns	8	318.61	
pH levels	2	1036.61	518.305**
Oat straw levels	2	1955.95	977.975**
Drainage levels	2	5794.10	2897.05**
pH x oat straw levels	4	342.05	85.5125**
pH x drainage levels	4	1108.33	277.083**
Oat straw x drainage levels	4	657.68	164.920**
pH x oat straw x drainage levels	4	1051.97	262.493**
Error	42	777.99	18.524

The highly significant interactions of drainage levels with pH and oat-straw levels indicates that the over-all trend may not be maintained at all pH and oat-straw levels. The interaction effects have not been subjected to further statistical analysis. A precise evaluation of these effects is therefore not possible. But a sufficiently clear indication of the trends is given by the figures which are presented below.

The nature of the oat straw x drainage level interaction may be gauged from Fig. 26 and from the following figures:

WEIGHT OF STRAW IN GM.

Oat Straw Level	Well Drained	Submerged with Drainage	Submerged No Drainage
0.0 percent	354	542	555
0.2 "	326	488	453
0.4 "	289	478	360

The effect of increasing the level of oat straw is to decrease the yield of rice straw at all three levels of drainage. The effect is most marked and almost linear in the submerged no-drainage treatments, less so in the well drained soils and hardly perceptible and probably not significant in the submerged, with drainage treatments. It will be recalled that levels of iron and manganese after the initial period of rapid adjustment showed identical trends. The interesting features of this interaction are that the difference between the well drained and submerged, no-drainage treatments is exaggerated in the absence of oat straw and narrowed as the oat-straw level increases; and the benefits of drainage in the case of the submerged treatments are appreciable only at the highest level of oat straw.

The highly significant interaction between drainage and pH levels suggests that the influence of drainage levels may be different at different pH levels. That this is indeed the case is shown by Fig. 27 and by the following figures:

pH	Well drained	Sub. with drainage	Sub. no drainage
4.6	332	467	351
5.7	326	529	524
6.0	311	512	493

It is clear that well drained treatments are inferior to the submerged ones at all three pH levels but the inferiority is greatly

exaggerated at the two higher pH levels. There is a suggestion, also, of a tendency for yields to decrease as pH increases, in the well drained treatments. It is also apparent from the figures -- more so from Fig. 27 -- that though the submerged, with-drainage treatment is on the whole superior to the no-drainage treatment the superiority is limited almost entirely to the pH 4.9 treatment. At this pH, drainage has undoubtedly increased the yields in the submerged treatments. At the two higher pH levels there is no apparent difference between the submerged with and without drainage treatments.

The most important conclusion from the study of the pH x drainage interaction is that drainage has proved extremely beneficial *in the submerged treatments at pH 4.9.*

Oat Straw Levels. The analysis of variance (Table 9) indicates that the oat-straw level is the second most important factor influencing yields. On partitioning the sums of squares associated with this factor between its two components it becomes clear that the bulk of it is due to differences between the no-oat-straw treatment on the one hand and the two oat-straw treatments on the other. The highly significant mean square for the comparison between the two oat-straw levels suggests that increasing the level of oat straw from 0.2 percent to 0.4 percent also has had a real influence on yield.

Partition of Oat Straw Level Sums of Squares

	Degrees of Freedom	Sum of Squares	Mean Square
Oat straw levels	2	1955.95	
No oat straw vs. (0.2% + 0.4% oat straw)	1		1592.99**
0.2 percent vs. 0.4 percent oat straw	1		362.96**

The over-all effect of oat straw is to decrease yields as the following figures indicate:

Oat Straw Level	Yield of Straw from 27 pots (gm.)
0.0 percent	1451
0.2 "	1267
0.4 "	1127

The highly significant oat straw x drainage levels and oat straw x pH levels interactions suggest that the influence of oat straw may not be consistent at different drainage levels and pH levels. The oat straw x drainage levels interaction has already been discussed and is depicted in Fig. 26. The oat straw x pH level interaction remains to be considered.

$$r = -0.831^{**} = 0.077$$

$$Y = 71.0 - 0.153 X$$

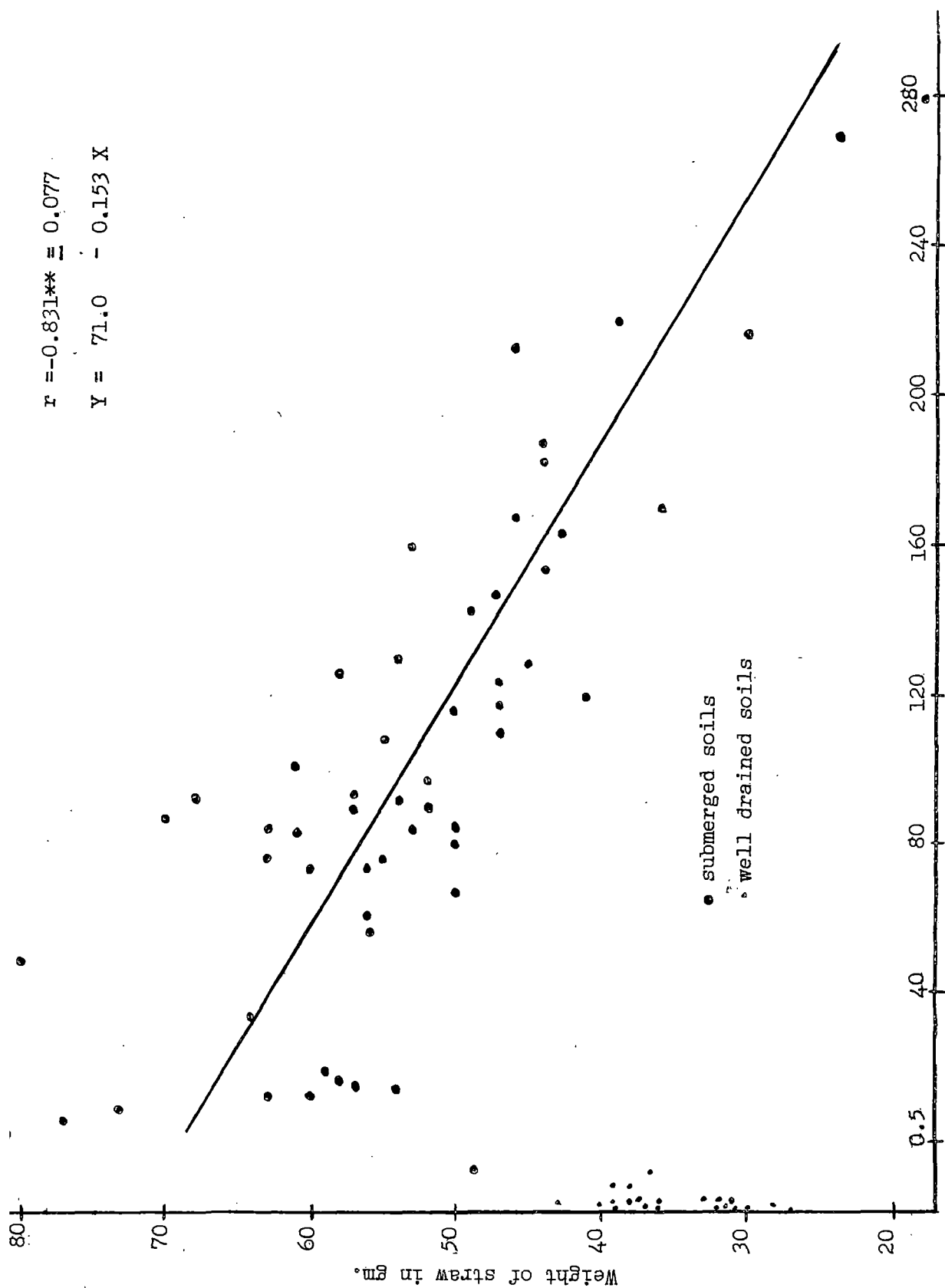
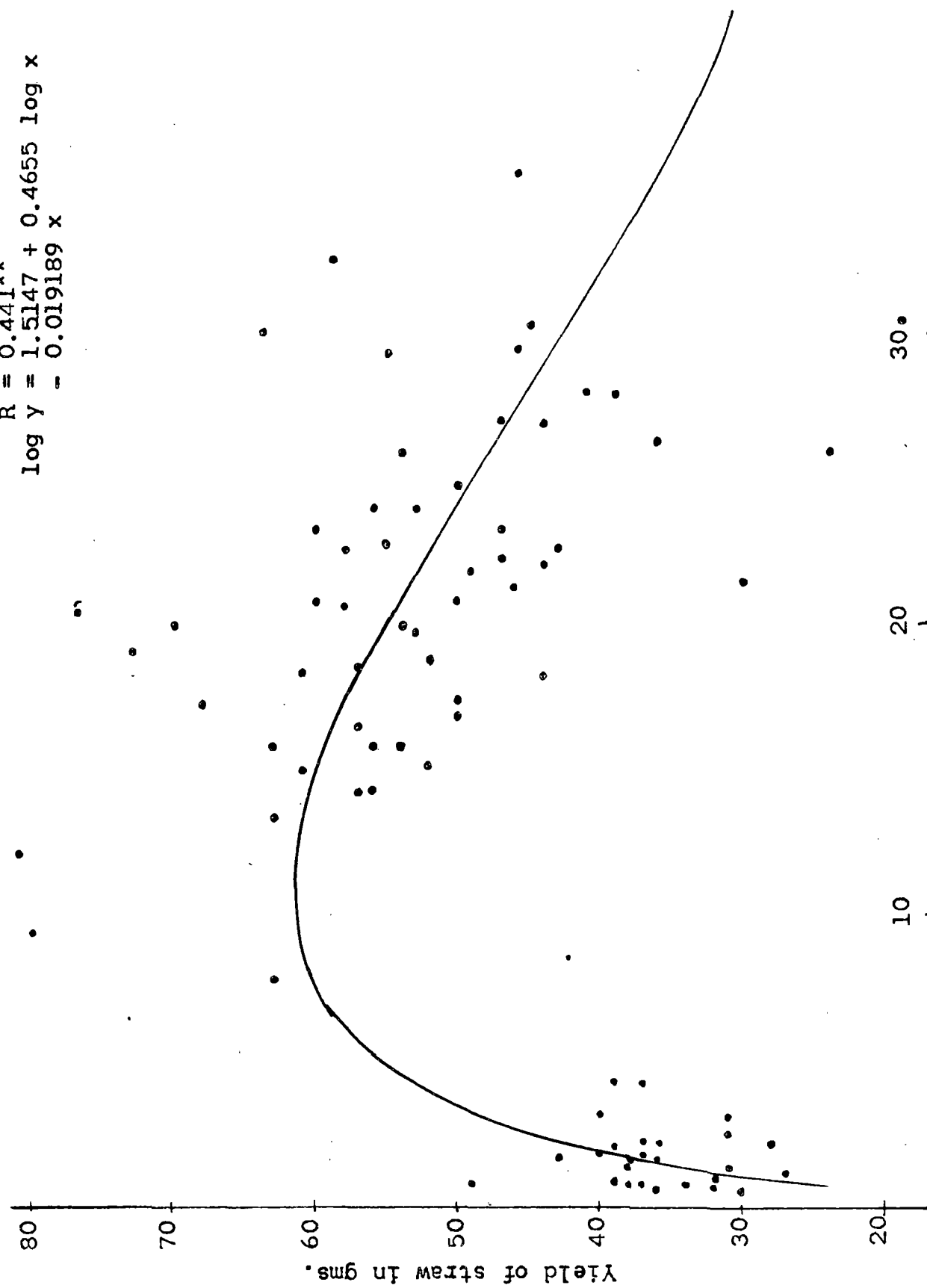


Fig. 23: Correlation between yield of straw and Iron in percolates taken 34 days from the start.

$$R = 0.441^{**}$$

$$\log y = 1.5147 + 0.4655 \log x$$

$$- 0.019189 x$$



ml. of 0.01 N KMnO_4 per 10 ml. of percolates taken 36 days from start

Fig. 24. Correlation between yield of straw and oxidizable matter.

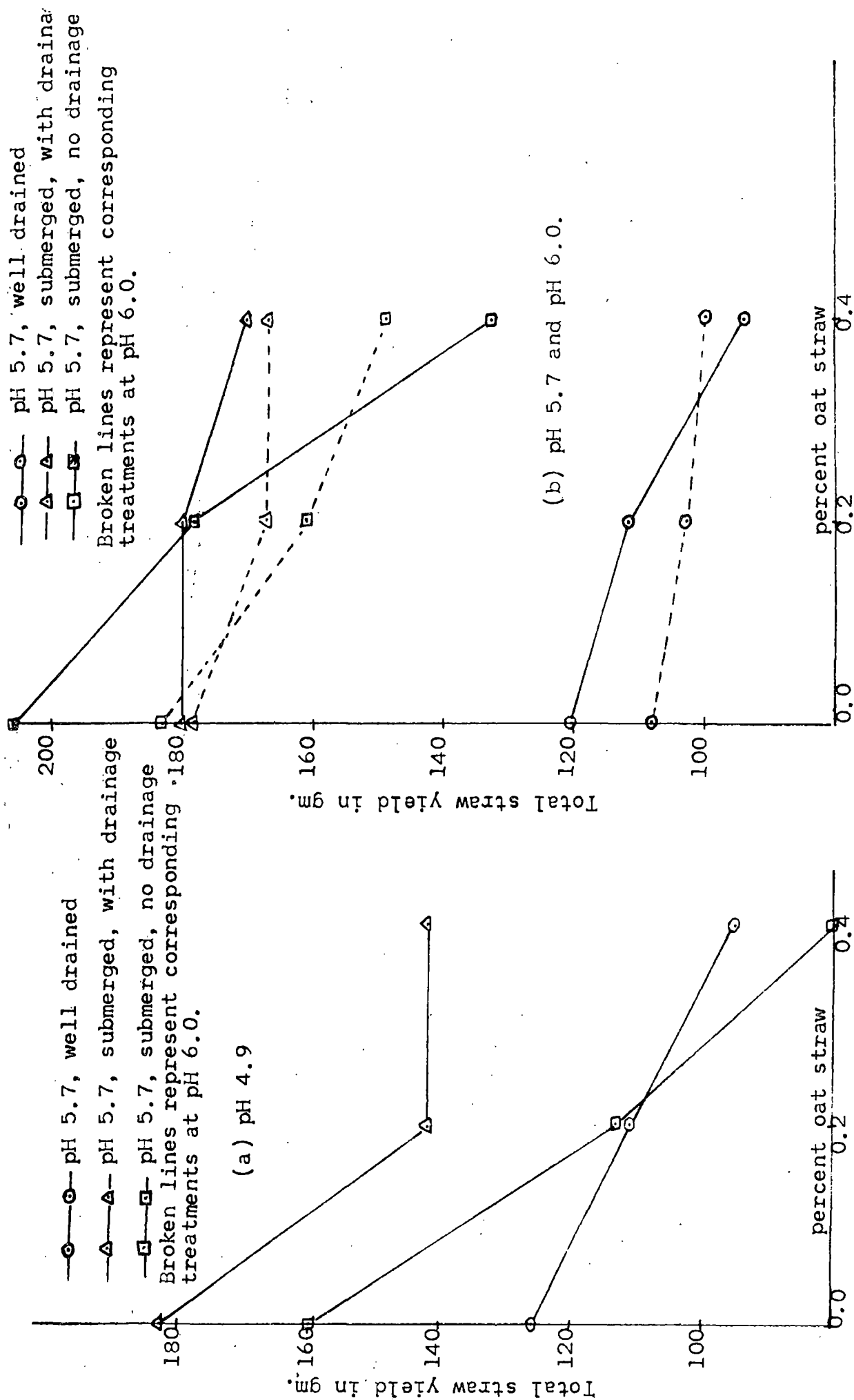


Fig. 25. Effect of oat straw level on straw yields.

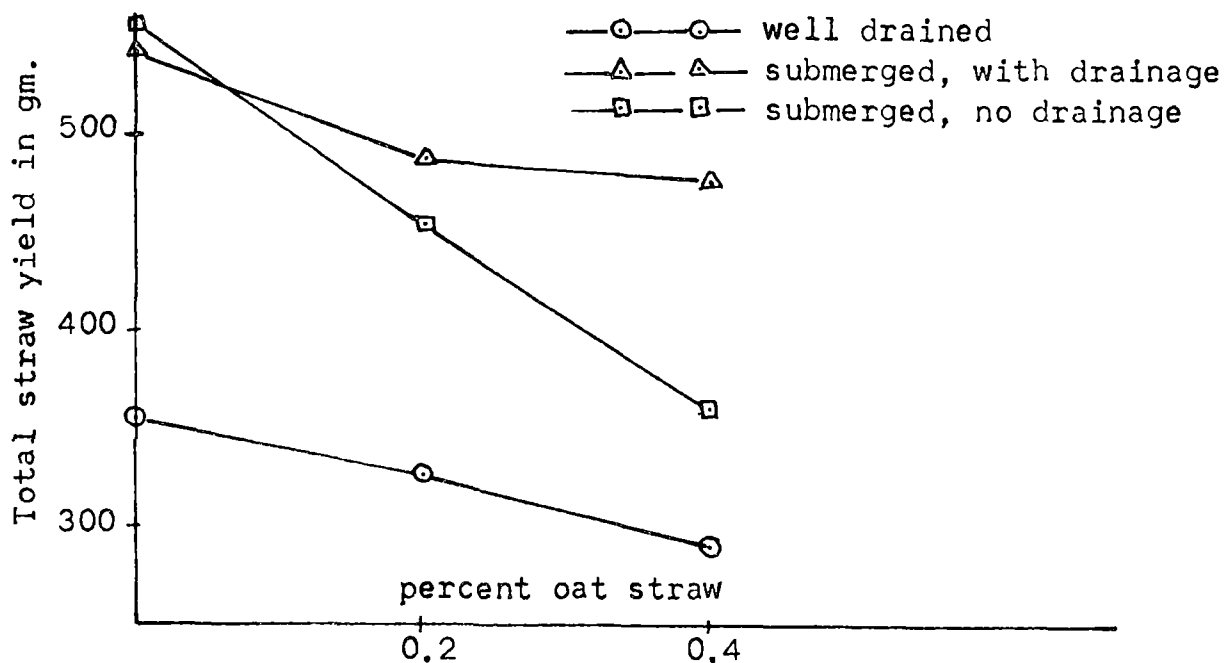


Fig. 26. Effect of oat straw level on straw yield over pH level

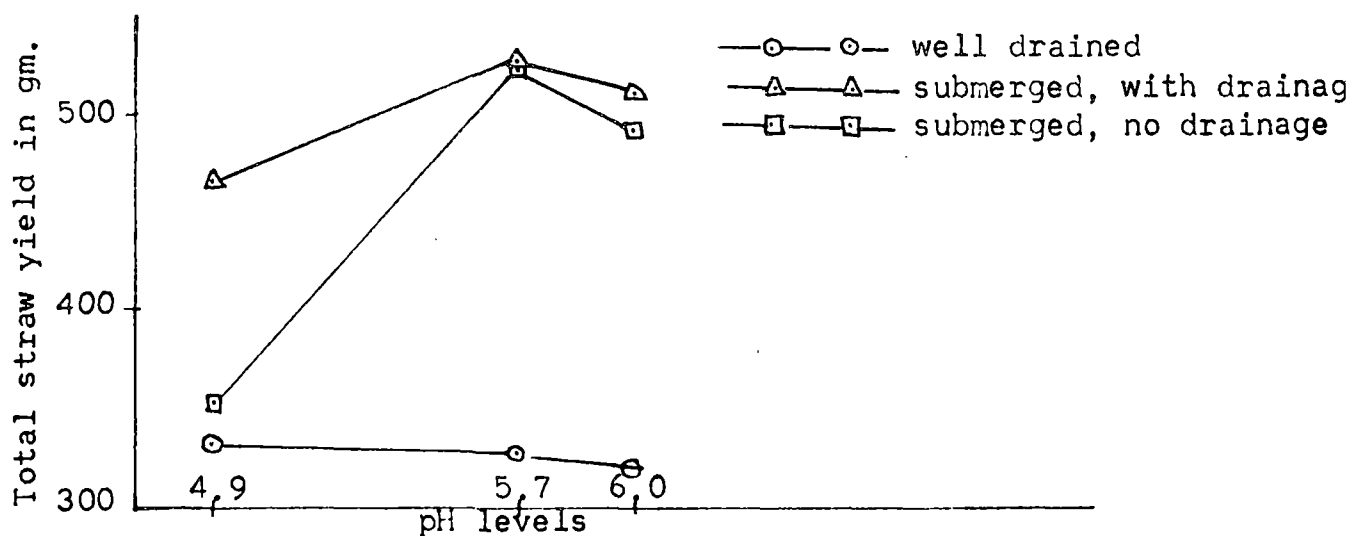


Fig. 27. Effect of pH level on straw yield over oat straw level

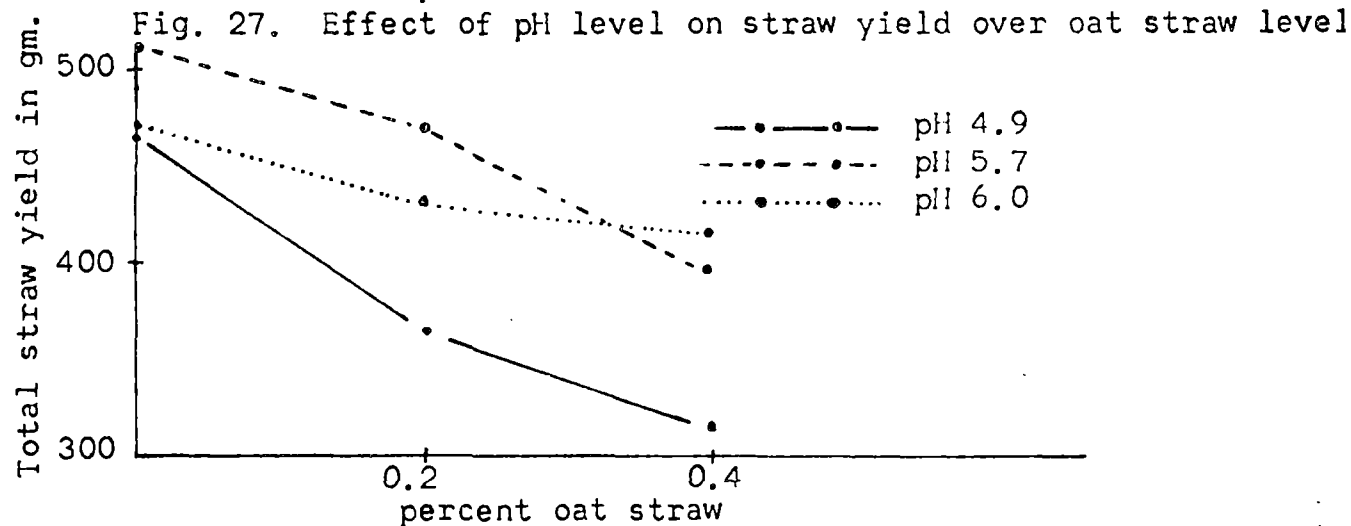


Fig. 28. Effect of oat straw level on straw yield over drainage levels

The oat-straw x pH interaction is represented graphically in Fig. 28. Numerical values of the yields at the three pH and oat straw levels are given below.

Oat Straw	Yield of Straw from 9 pots (gm.)		
	pH 4.9	pH 5.7	pH 6.0
0.0 percent	469	512	470
0.2 "	366	470	431
0.4 "	315	397	415

The figures and the graph show that increasing the level of oat straw depresses yields at all three pH levels. The effect is marked at pH 4.9 and 5.7.

pH Levels. The effect of pH levels on yield is highly significant but the bulk of the variability associated with pH levels lies between pH 4.6 on the one and the two higher pH levels on the other as the following figures indicate.

Partition of pH level Sums of Squares			
Source	Degree of Freedom	Sums of Squares	Mean Square
pH levels	2	1036.61	
pH 4.7 vs. (pH 5.7 + pH 6.0)	1		963.11**
pH 5.7 vs. pH 6.0	1		73.500

The comparison between the two higher pH levels just falls short of significance at the 5 percent level. The treatment totals at each pH level are given below.

pH	Straw Yields from 27 Pots (gm.)
4.9	1150
5.7	1379
6.0	1316

These figures show that pH 4.9 is on the whole markedly inferior to the two higher pH levels between which there seems to be no real difference.

The highly significant interactions of pH levels with drainage and organic matter levels have already been discussed and are depicted in Figures 27 and 28. The beneficial effect of increase in pH from 4.9 to 5.7 on straw yields is obvious in the case of the submerged soils, especially those without drainage. The unfavorable effect of increase in oat straw is marked at the pH levels of 4.9 and 5.7.

The individual treatments. A study of the individual treatment yields brings out more clearly the simple effects of the three treatment factors, pH, oat straw, and drainage levels. It also facilitates an interpretation of these effects in terms of the chemical and physico-chemical analyses. The 27 individual treatment totals are given in the accompanying table.

TABLE 10
TOTAL STRAW YIELDS OF INDIVIDUAL TREATMENTS

Drainage	Well Drained			Submerged, with Drainage			Submerged, No Drainage		
Oat Straw %	0.0	0.2	0.4	0.0	0.2	0.4	0.0	0.2	0.4
pH									
4.9	126	111	95	183	142	142	160	113	78
5.7	120	112	94	180	179	170	212	179	133
6.0	108	103	100	179	167	166	183	161	149

The significance of the differences among the treatment means is shown in Table 11.

It is convenient to consider the individual treatments by the drainage classes.

The well drained treatments. Among these treatments, the most striking effects are those of increase in pH at the 0.0 percent oat-straw level and of oat straw at pH 4.9 and 5.7. At the 0.0 percent oat-straw level the yield of straw decreases as the pH increases from 4.9 to 6.0. The only significant* difference, however, is that between the two extreme pH levels. This decrease in straw yield may be attributed to decrease in availability of iron as the pH level increases. The

* Means significant at the 5 percent level.

accompanying table shows that the level of available iron was consistently higher in the well drained soils at pH 4.9 than at pH 6.0, during the growing season.

pH	Fe in Morgan's Extracts on Days from Start		
	18	37	70
	(lbs. per acre)		
4.9	44	37	98
6.0	29	15	44

At the pH levels of 4.9 and 5.7 the straw yield decreases as the oat-straw level rises but once again only the differences between the extremes are significant. The decrease in yield with increase in oat-straw level at pH 4.9 may be ascribed to nitrogen deficiency. As mentioned earlier both oat-straw treatments at pH 4.9 showed chlorotic symptoms. Chemical analyses lend support to this view. The chemical analyses showed similar trends at pH 5.7 although the plants showed no marked chlorosis.

Submerged, with drainage treatments. The study of the interaction effects of drainage with pH and oat-straw levels (Figs. 26 and 27) indicated that there were no marked differences among the submerged treatments. The detailed figures for the individual submerged treatments largely confirm this for the only significant differences are between the 0.2 oat-straw treatments of pH 4.9 and 5.7, and between the lowest and highest levels of oat straw at pH 4.9. The latter is due to an inexplicable chemical phenomenon in one of the replicates of the 0.0 percent oat-straw treatment, while the former appears to have some chemical basis.

The first point that requires comment is the apparent uniformity of the yields in the pH 5.7 and 6.0 treatments despite differences in oat-straw level. It will be recalled that a similar uniformity was evident in the chemical analyses of the submerged, with drainage treatments. This uniformity may be attributed to the levelling effect of drainage on pH and oat-straw effects. The levelling effect springs from the removal in the drainage of reduced products, chiefly Fe^{+2} and Mn^{+2} , which otherwise would accumulate in amounts varying according to treatment factors.

Although drainage can prevent the accumulation of Fe^{+2} and Mn^{+2} it cannot nullify solubility relationships governed by pH. Thus the concentration of soluble Fe^{+2} and Mn^{+2} would tend to increase as pH level decreases, provided a reserve of reduced iron and manganese in the solid phase is present. This may be the reason for the lower yields in the 0.2 and 0.4 percent oat-straw treatments of pH 4.9 than in the corresponding treatments at the higher pH levels. Chemical analyses of the percolates provide ample confirmation of this: throughout the growing

TABLE 11
SIGNIFICANCE OF DIFFERENCES AMONG INDIVIDUAL TREATMENTS
(STRAW YIELDS) BY THE DUNCAN MULTIPLE RANGE TEST*

Treatment No.	pH	Treatment		Mean Yield (gm.)	
		Oat Straw %	Drainage		
XII	5.7	0.0	s.n.d.	70.7	**
XXI	6.0	0.0	s.n.d.	61.0	
II	4.9	0.0	s.w.d.	61.0	
XI	5.7	0.0	s.w.d.	60.0	
XIV	5.7	0.2	s.w.d.	59.7	
XV	5.7	0.2	s.n.d.	59.7	
XX	6.0	0.0	s.w.d.	59.7	
XVII	5.7	0.4	s.w.d.	56.7	
XXIII	6.0	0.2	s.w.d.	55.7	
XXVI	6.0	0.4	s.w.d.	55.3	
XXIV	6.0	0.2	s.n.d.	53.7	
III	4.9	0.0	s.n.d.	53.3	
XXVII	6.0	0.4	s.n.d.	49.7	
V	4.9	0.2	s.w.d.	47.3	
VIII	4.9	0.4	s.w.d.	47.3	
XVIII	5.7	0.4	s.n.d.	44.3	
I	4.9	0.0	w.d.	42.0	
X	5.7	0.0	w.d.	40.0	
VI	4.9	0.2	s.n.d.	37.7	
XIII	5.7	0.2	w.d.	37.3	
IV	4.9	0.2	w.d.	37.0	
XIX	6.0	0.0	w.d.	36.0	
XXII	6.0	0.2	w.d.	34.3	
XXV	6.0	0.4	w.d.	33.3	
VII	4.9	0.4	w.d.	31.7	
XVI	5.7	0.4	w.d.	31.3	
IX	4.9	0.4	s.n.d.	26.0	

* Duncan, D. B. Multiple Range and Multiple F Tests. Tech. Rep. No. 6a. Virginia Polytechnic Institute. 1953.

** Any two means not included in the same line are significantly different at the 5 percent level. Any two means included in the same line are not significantly different at the 5 percent level.

season iron and manganese were higher in the submerged, drainage treatments of pH 4.9 than at the two higher pH levels.

The behavior of the 0.0 percent oat-straw, pH 4.9 treatment runs counter to both the principle of equalization of chemical composition of percolates and the solubility relationships just referred to. This anomaly is due to the extraordinarily good growth of the plants in one replicate of this treatment. Chemical analyses revealed a higher nitrate concentration and lower iron and manganese concentrations in this pot than in the two other replicates, during the early part of the growing season. The following figures bring out the association clearly:

Days from start			17			34		
Pot No.	Replicate	Straw Yield (gm.)	NO ₃ ¹	p.p.m. Fe	Mn	NO ₃ ¹	p.p.m. Fe	Mn
4	1	54	-	-	-	0.1	130	20.5
5	2	80	9.0	36.5	11.3	0.1	48.1	9.5
6	3	49	0.6	52.5	11.9	0.1	143	21.0

But for the unusual behavior of replicate 2 the yield from this treatment would probably have been substantially the same as at the two higher oat-straw levels at the same pH. When allowance is made for this peculiar behavior, the conclusion appears inescapable that the lower yields in the pH 4.9 treatments than in the higher pH treatments may be associated with a higher concentration of Fe⁺² and Mn⁺².

The submerged, no-drainage treatments. The most striking differences due to pH and oat-straw treatments are found in the submerged no-drainage treatments. The accumulation of reduced substances to the fullest extent permitted by the treatment factors and the absence of nutrient losses by leaching combine to make these treatments eminently suitable for the comparison of the effects of reduced substances on the growth and yield of the rice plant. It is not surprising, therefore, to find that all but two of the eighteen comparisons possible within pH levels and within oat-straw levels in this group of treatments are significant.

The effect of increasing the oat-straw level is to decrease the yield. The decreases are significant at all successive levels of pH and oat straw except between the 0.2 percent and 0.4 percent oat-straw levels at pH 6.0. The decreases due to increase in oat straw are most pronounced at pH 4.9, less so at pH 5.7, and least at pH 6.0. These effects are represented graphically in Fig. 25 (a) and (b).

The effect of pH is not consistent. At all three oat-straw levels pH 4.9 is markedly inferior to pH 5.7 and 6.0. But the differences between the two higher pH treatments are neither marked nor consistent.

The chemical analyses exhibit a marked parallelism to these effects. The concentrations of iron and manganese were remarkably high in the percolates from the submerged soils with no drainage while the concentrations of these products were lower and not appreciably different from each other at the two higher pH levels. Also, the accumulation of soluble iron and manganese was intensified by successive additions of oat straw. (v. Figures 8-10.) It will be recalled that even in the submerged soils with drainage, where treatment differences tended to be ironed out, lower yields were associated with the lowest pH level -- the pH level at which the concentration of iron and manganese were highest for the soils with drainage. The conclusion is inevitable that an excess of iron and/or manganese was proving toxic to the rice plants.

There are several reasons for believing that excess iron is the toxic factor. First, the concentration of iron during the greater part of the growing season was about five times that of manganese; secondly, Fe^{+2} being more readily oxidized than Mn^{+2} by the oxygen exuded by rice roots could form a deposit on the root surface and impede mechanically and chemically the uptake of nutrients; finally comparison of the yield data with the chemical analyses revealed a closer association between yield and iron than with manganese. The next step is to attempt a quantitative correlation between yield and concentration of iron.

A quantitative correlation between yield and iron concentration is beset by two difficulties. First, the concentration of iron was never static during the growing season. Secondly, any retardation of growth by excess iron was no doubt confounded with differences in nutrient level caused by drainage in half of the submerged treatments. The first difficulty, though serious is not insuperable. It is clear from an examination of the graphs for the changes in concentration of iron during the growing season (v. Figs. 8-10) that for most treatments the concentration of iron for the greater part of the season got fairly stabilized around the level at 34 days after submergence. Notable exceptions are all the submerged, no-drainage soils of pH 4.9 and the no-oat-straw, submerged, no-drainage treatments of pH 5.7 and 6.0. The second difficulty could be eliminated by omitting the soils with drainage from the correlation. This would exclude the factor which more than anything else influenced the concentration of iron. All the submerged treatments are therefore included. Figure 23 reveals the high negative correlation between the yield of straw and the concentration of iron in the percolates for the 54 submerged pots.

Although the purpose of this diagram is to illustrate the decrease in yield with increase in iron concentration of the submerged soils, the variation of yield with iron concentration in the displaced soil solutions of the well drained soils is also represented. In the face of analytical difficulties in determining very small amounts of

iron and the small amplitude of the variations, no correlation was attempted between yield and iron. A slight tendency for yields to increase with increase in iron concentration is, however, perceptible. It will be recalled that a similar trend was demonstrated in a more convincing manner with the iron extractable in Morgan's reagent.

The rapid increase in yield with increase in iron concentration in the very low zone of concentrations and the slower decline in yield at the higher concentrations suggested that the equation $y = ax^b e^{-cx}$ would describe the response of yield to changes in iron concentration over the entire range. The concentrations of iron in the soil solutions from the well drained soils, however, were so low and subject to such a relatively high experimental error that the value of a quantitative correlation involving these values was doubted. The more tangible figures provided by the determination of the reducing capacity (oxidizable matter) of the soil solutions from the 81 pots were therefore used to fit statistically a curve of the type described by this equation and a highly significant correlation obtained. The results are represented graphically in Fig. 24. The curve suggests that there is a level of reduction at which the yield of rice plants would not be adversely affected by an inadequate supply of reduced substances on the one hand and an excess of them on the other. Under the conditions of the experiment this level of reduction may be characterized by a figure of approximately 10 ml. of 0.01 N $KMnO_4$ for oxidizable matter of the soil solutions taken 34 days from transplanting.

(b) Yield of Grain

The grain yields do not, unfortunately, reflect the treatment effects as well as the straw yields do. The obliteration of all except the most pronounced treatment effects is almost entirely due to the high and variable percentage of sterility. The sterility percentage followed no treatment trends though in certain treatments sterility was undoubtedly partly a function of treatment.

The absence of any marked treatment trends is evident from the sterility figures in Table 18 and more clearly from Table 17 of Appendix. The figures show that some of the widest variations in sterility percentage are found within rather than between treatments. Although low temperature and poor light at heading time, as indicated earlier, may be responsible for the high percentage of sterility, these factors do not account for the high variation within treatments in which the replicates headed and bloomed at about the same time. Whatever the explanation of the variation of sterility percentage within treatments there are additional reasons for believing that it was due to climatic and not soil factors.

In a preliminary experiment to test the feasibility of growing rice to maturity under Ithaca conditions in a greenhouse, many of the treatments in which final yield of grain was seriously affected by sterility showed no detectable sterility. There was, however, one important difference: in this experiment rice was seeded on March 7, grew under

artificial light in early spring and bloomed under the favorable light and temperature conditions of the third week of July. In the subsequent experiment rice seeded on April 17 and harvested in the first week of October, likewise, showed no appreciable sterility. The high percentage of sterility in rice that came into the second week of October in the experiment presently under discussion may therefore be attributed to unfavorable climatic conditions.

The high and variable percentage of sterility tended to mask many otherwise obvious differences in grain yields. Another factor narrowed still further the absolute differences among treatments: poorly filled grain (due to light of low intensity and short duration during the period of maturation) made the final yields of grain very low indeed. These figures are given in Tables 17 and 18 of the Appendix, and the analysis of variance in Table 12 on page 146.

The analysis of variance shows that of the main and interaction effects only drainage and the pH x drainage interaction are significant. These are significant at the one percent level. It is also apparent that differences due to the drainage treatments and random variations account for a high proportion of the sums of squares. Also the high value of the error mean square gives this experiment a coefficient of variation of nearly 30 percent.

The drainage sums of squares may be apportioned to its sources as follows:

Partition of Drainage Sums of Squares

Source	Degrees of Freedom	Sums of Squares
Drainage levels	2	2768.83
Well drained vs. submerged	1	2763.55**
Submerged with drainage vs. submerged, no drainage	1	4.68

Obviously, the comparison between the well drained treatments and the submerged treatments taken as a class account for almost the entire variability due to drainage treatments. The following figures show the gulf between the well drained and the submerged treatments:

Drainage level	Yield of grain from 27 pots (gm.)
Well drained	281.9
Submerged, with drainage	624.4
Submerged, no drainage	608.5

TABLE 12
ANALYSIS OF VARIANCE OF GRAIN YIELDS

Source	Degrees of Freedom	Sum of Squares	Mean Square
Rows	8	237.55	
Columns	8	188.41	
pH levels	2	29.37	14.685
Oat straw levels	2	48.95	24.475
Drainage levels	2	2768.23	1384.1**
pH x oat straw levels	4	107.05	26.763
pH x drainage levels	4	621.75	155.44**
Oat straw x drainage levels	4	213.36	53.340
pH x oat straw x drainage levels	4	141.57	35.393
Error	42	1080.88	25.735

The grain yields show the same trends as the straw yields with two differences: first, the gap between the well drained and submerged treatments has been widened; secondly, the difference between the two submerged treatments has been narrowed to the point that the submerged with drainage treatment is no longer superior (statistically) to the no-drainage treatment.

The intensification of the inferiority of the well drained treatments to the submerged ones where grain yields are concerned is easy to understand. It will be recalled that during the greater part of the period of vegetative growth the well drained treatments excelled the submerged treatments. It was only the dramatic recovery of the submerged treatments at the time of heading that enabled them to outyield the well drained treatments in weight of straw. With grain yields, however, everything seemed to favor the submerged treatments. They staged a rapid recovery at heading time while the well drained treatments stagnated; they generally headed earlier and produced large panicles; abortion of florets did not occur in the submerged treatments (except one diseased treatment) as it did in the well drained treatments. Thus the superiority of the submerged treatments to the well drained treatments was enhanced when it came to grain yields.

In the absence of significance even at the 5 percent level pH levels and oat-straw levels are omitted from the discussion. The highly significant pH x drainage levels interaction, however, merits analysis.

The interaction has not been analyzed further but Fig. 29 and the accompanying table give a sufficiently clear idea of the trends.

pH	Yield of grain from 9 pots (gm.)		
	well drained	submerged with drainage	submerged no drainage
4.9	126.1	204.1	155.8
5.7	91.3	222.4	213.0
6.0	64.5	198.9	239.7

The graph brings out even more clearly than the table the marked decrease in yield in the well drained treatments as pH increases and the almost linear increase in yield with pH in the submerged no-drainage treatments. The submerged treatments with drainage are not appreciably affected by pH changes. The trends are analogous to those of straw yields (v. Fig. 27) but the decrease in yield with increase in pH is accentuated. Evidently increase in pH in the well drained soils has a much more adverse effect on grain yield than on straw yield. Quantitative data were not necessary to prove this point for it was obvious from the behavior of the plants at the time of heading.

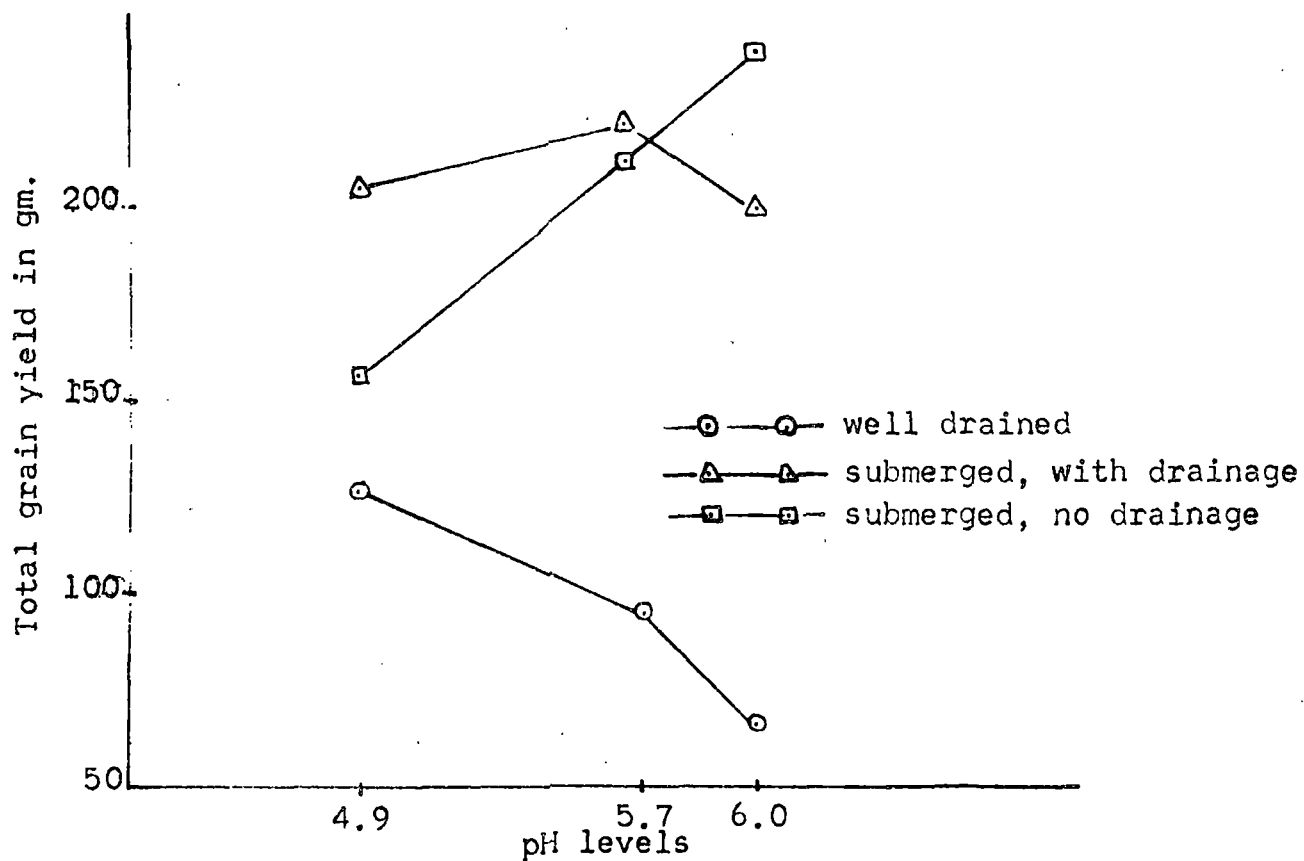


Fig. 29. Effect of pH level on yield of grain at the three drainage levels.

It will be recalled that though the well drained treatments at pH 4.9 suffered a retardation of growth which was common to all the well drained treatments they produced apparently normal panicles. The well drained treatments at pH 5.7 and 6.0 on the other hand headed later and with difficulty and gave thin narrow panicles with a high proportion of aborted florets. Apparently the well drained soils at the higher pH levels lacked a factor present in abundance in the submerged soils and only in threshold amounts in the well drained soils of pH 4.9, which played an important part during the reproductive phase. The chemical analyses pointed to iron as the critical factor; physiological considerations support this.

The reproductive phase in plants is a time of intense metabolic activity and is marked by increased respiration. Since the iron-containing heme-protein pigments, the cytochromes, play such an important part as electron carriers in aerobic respiration it is not unreasonable to suppose that an insufficiency of iron may preclude maximum respiration and thereby retard the metabolic changes associated with the reproductive phase.

Individual treatments. The individual treatment totals are given in Table 13. The simple effects of pH, oat-straw level and drainage level may be studied with the help of these figures.

TABLE 13
TOTAL GRAIN YIELDS (IN GM.) FROM INDIVIDUAL TREATMENTS.

Drainage	Well Drained			Submerged, with Drainage			Submerged, no Drainage		
Oat Straw %	0.0	0.2	0.4	0.0	0.3	0.4	0.0	0.2	0.4
pH									
4.9	38.2	43.3	44.6	60.6	68.0	75.5	69.8	49.8	36.2
5.7	25.8	37.4	28.1	92.2	62.6	66.6	79.5	72.7	60.8
6.0	21.5	13.2	29.8	62.1	61.2	75.6	84.6	78.3	76.8

These figures in general confirm the treatment trends manifested by the straw yields though the relative differences among treatments have been considerably modified. The exceptional behavior of a small number of the treatments can be shown to be associated with the

sterility percentage. The significant differences are shown in Table 14.

In the well drained class, as with straw, grain yields decrease with increase in pH level at all three levels of oat straw. Only the differences between the extreme levels of pH however are significant. Increase in level of oat straw decreased straw yields at all three pH levels. The erratic influence of oat-straw levels on grain yields is clearly associated with variations in the sterility percentage as the figures of Table 18 of Appendix indicate.

In the submerged, with drainage treatment there are no significant differences within a pH level or within an oat-straw level except in the comparisons with the 0.0 percent oat-straw, pH 5.7 treatment. The unusually high yield in this treatment is due to the comparatively low sterility percentage in two of the replicates.

The most marked and numerous differences, as with the straw yields, are found in the submerged, no-drainage group of treatments. Though not all differences are significant the trends along both pH and oat-straw levels are quite consistent. As with the straw, the yields increase as the pH increases within an oat-straw level and decrease as the oat-straw level increases within a pH level. The depressing effect of oat straw on yields is once again most pronounced at pH 4.9, less so at pH 5.7 and least at pH 6.0.

It is clear that despite the high variability in the sterility percentage grain yields run a course which with few exceptions is parallel to the straw yields.

Yield of Roots. The yield of roots from each of the 81 pots is given in Table 17 of the Appendix and the mean yields for each treatment, in Table 18 also of the Appendix.

The yields of roots show an amazing parallelsism to the yields of straw. In all but the well drained treatments at pH 5.7 and 6.0 and also the submerged, no-drainage, 0.4 percent oat-straw treatment at pH 4.9, the straw: roots ratio is uniformly 2:1. In the few exceptional treatments -- the poorest by all standards -- the ratio is approximately 3:1.

The very unfavorable effect of high pH on root growth in a well drained soil is illustrated by the contrasts among Plates I, II and III.

There were striking differences in the appearance of the roots. As with the quantitative yield data the most obvious difference was between the well drained and the submerged treatments.

The submerged treatments, with the exception of the pH 4.9; 0.4 percent oat-straw, no-drainage treatment, had reddish-brown, well

TABLE 14
SIGNIFICANCE OF DIFFERENCES AMONG TREATMENT MEANS
(Grain Yields)

Treatment No.	Treatment			Mean Yield Grain (gm.)
	pH	Oat Straw %	Drainage	
XIV	5.7	0.2	s.w.d.	30.87*
XI	5.7	0.0	s.w.d.	30.73
XXI	6.0	0.0	s.n.d.	28.20
XII	5.7	0.0	s.n.d.	26.50
XXVII	6.0	0.4	s.n.d.	26.27
XXIV	6.0	0.2	s.n.d.	26.10
XXVI	6.0	0.4	s.w.d.	25.20
VIII	4.9	0.4	s.w.d.	25.17
XV	5.7	0.2	s.n.d.	24.23
III	4.9	0.0	s.n.d.	23.27
V	4.9	0.2	s.w.d.	22.67
XVII	5.7	0.4	s.w.d.	22.20
XX	6.0	0.0	s.w.d.	20.70
XXIII	6.0	0.2	s.w.d.	20.40
XVIII	5.7	0.4	s.n.d.	20.27
II	4.9	0.0	s.w.d.	20.20
VI	4.9	0.2	s.n.d.	16.60
VII	4.9	0.4	w.d.	14.87
IV	4.9	0.2	w.d.	14.43
I	4.9	0.0	w.d.	12.73
XIII	5.7	0.2	w.d.	12.47
IX	4.9	0.4	s.n.d.	12.07
XXV	6.0	0.4	w.d.	9.93
XVI	5.7	0.4	w.d.	9.37
X	5.7	0.0	w.d.	8.60
XIX	6.0	0.0	w.d.	7.17
XXII	6.0	0.2	w.d.	4.40

* The difference between any two means within a line is not significant at the 5 percent level.

developed root systems with a mat of fine white roots at the surface. The reddish-brown color no doubt was due to the oxidation and deposition of ferric hydroxide on the surface of the roots. In sharp contrast to the profuse, reddish-brown, soft-textured roots of the majority of the submerged treatments, the root systems of the pH 4.9, 0.4 percent oat-straw, no-drainage treatment (and to a lesser extent the 0.2 percent oat-straw treatment at the same pH and drainage levels) were scanty in extent, dark brown in color, and coarse in texture. Besides, the mat of fine white roots at the surface, and branched roots below, were absent. No histological studies were made on the roots but the coarser texture and the darker color than in the healthy root systems suggest that these roots were heavily encrusted with ferric oxides.

It will be recalled that this is the treatment in which growth and yield were poorest among the submerged treatments and the symptoms provisionally attributed to iron toxicity were most pronounced. It will also be recalled that similar symptoms were associated with a physiological disease of rice called "mentek" in Java.

Van der Elst, cited by Van der Vecht (240), believed that the disease was due to oxygen deficiency in the roots. Kuilman (142) attributed the disease to a poor root system coupled with potassium deficiency. Van der Vecht (240) suggested that it was due to a nematode infestation of the roots. In the light of the results of the present investigation it would appear that the poor root development is a consequence of the presence of an incredibly high concentration of reduced iron in the root environment. The retardation of growth and the deficiency of potassium within the plant may be a consequence of the inability of the encrusted roots to function efficiently as an absorbing organ for nutrients while the nematode infestation may be a secondary effect following the loss of vigor of the roots.

In contrast to the profuse, reddish-brown, moderately branched root systems of the majority of the submerged treatments, those of the well drained treatments were scanty, white in color, and highly branched. Further, the fine superficial root system was entirely absent. Among the well drained treatments themselves, there was the striking contrast between the root systems of the pH 4.9 treatments on the one hand and the pH 5.7 and 6.0 treatments on the other. The root systems of the pH 4.9 treatments were far better developed, were gleaming white in appearance, and profusely branched below a depth of about 3 inches. The roots systems from the higher pH treatments were extremely poorly developed, coated with clay particles, but well branched. Apparently, the soils with the higher pH values were a very unfavorable environment for the development of roots by the rice plants.

4.4 General Discussion and Conclusions

The evidence is clear that a submerged soil is a better medium for the growth and yield of rice (variety, Zenith) than a well drained

soil. The superiority of a submerged soil as a milieu for rice appears to be associated chiefly with increased availability of iron as a result of the reduction process. There is very clear evidence also that an excess of reduced substances, among them probably iron, is injurious to rice. The postulates with which this experiment was started have thus been confirmed.

The purpose of the experiment was to grow rice over a sufficiently wide range of reducing conditions and to characterize chemically and physico-chemically the range of reducing conditions in which rice would not be adversely affected by a deficiency of iron on the one hand and an excess of reduced products on the other. In the chemical characterization, the most useful single property was the concentration of iron in the soil solution, while the three physico-chemical properties, pH, specific conductance, and redox potential, all showed some merit under the conditions of this experiment.

Growth of rice, more particularly yield of grain was lowest in the well drained soils as a group. Chemically these soils were characterized by extremely low concentrations of iron, manganese and oxidizable matter in the soil solution. Among these soils, best growth and yield was associated with those in which the iron extractable with Morgan's reagent was highest throughout the growing season. In all the well drained soils redox potentials were very high during the entire growing season while the pH was lower than for the submerged soils especially during the latter part of the growing season.

The two highest yields of straw and the third and fourth highest yields in grain (despite the high variability in sterility) were from the no-oat-straw, submerged no-drainage treatments at pH 5.7 and 6.0 as Tables 13 and 14 indicate. Chemically these treatments were characterized by a high concentration of nitrate and relatively low concentrations of iron and manganese during the first 34 days of the growing season. In sharp contrast to these high yielding treatments were the 0.4 percent oat-straw, no-drainage treatments at pH 4.9 and 5.7. These treatments produced the two lowest yields of straw and one of them also the lowest yield of grain among the submerged treatments. (v. Tables 13 and 14.) Is it purely fortuitous that two of the highest concentrations of iron during the greater part of the growing season were associated with them? The contrast between these treatments and the two good treatments mentioned above is brought out in Table 15.

These figures suggest that under the conditions of this experiment the highest yielding treatments are characterized by a relatively low concentration of iron in the soil solution during the early part of the growing season.

The physico-chemical properties, too, are not without value in characterizing the best treatments among the submerged soils. Conductance and pH values in themselves are of little use but it can be

shown that the better treatments were associated with a relatively slow increase in pH and a relatively slow decrease in conductance. Redox potential however appears to be the best diagnostic tool among the physico-chemical properties. The best treatments were characterized by a relatively high redox potential during the early part of the growing season as the figures in Table 16 indicate. It must, however, be emphasized that a low redox potential per se was not found to be unfavorable to rice. Some of the better yielding treatments in fact had low redox potentials almost from the start. But these were the treatments in which the removal of reduced products in the drainage prevented high concentrations of soluble iron and manganese from being built up. This does not detract from the great value of redox potential as an index of the state of reduction of a soil. And if a relatively low iron concentration (for a submerged soil) is best suited to the growth of rice, as already suggested a high redox potential may be taken as a safe index of productivity of a rice soil in the absence of unfavorable factors not associated with the reduction process in submerged soils.

It is imprudent to make sweeping generalizations from the limited study on a single variety of rice on a single soil type under a single set of climatic conditions. It may, however, be indicated that: (i) a combination of the factors, very poor drainage, high organic matter content, and low pH, is unfavorable to rice; (ii) the unfavorable effects of low pH and high organic matter content may be ameliorated by a moderate amount of drainage; (iii) a high nitrate content is favorable to the growth of rice, whatever the mechanism of its action; and (iv) a low pH is favorable to rice under upland conditions.

TABLE 15
INFLUENCE OF CHEMICAL COMPOSITION OF SOIL SOLUTION ON THE YIELD OF RICE

Treat- ment No.	Treatment		No. of Tillers	Straw gm.	Grain gm.	Roots gm.	Days from Transplanting											
	pH	Oat Straw %					17			34			67			p.p.m.		
							NO ₃	Fe	Mn	NO ₃	Fe	Mn	NO ₃	Fe	Mn	NO ₃	Fe	Mn
XII	5.7	0.0	s.n.d.	29.3	70.7	26.50	30.0	263	3	8	128	8	19	0.1	97	27		
XXI	6.0	0.0	s.n.d.	32.3	61.0	28.30	30.0	193	3	7	1	21	22	0.1	93	36		
IX	4.9	0.4	s.n.d.	10.0	26.0	12.07	10.3	30*	117	38	0.1	240	45	0.1	474	55		
XVIII	5.7	0.4	s.n.d.	14.0	44.3	20.27	19.0	43	40	21	0.1	167	46	0.1	180	40		

* High figure due to the inexplicable presence of 90 p.p.m. NO₃ in one of the replicates.

TABLE 16
INFLUENCE OF REDOX POTENTIAL ON YIELD OF RICE

Treatment No.	E _G in Millivolts on Days from Transplanting						
	1	3	5	8	16	32	65
XII	374	289	216	242	124	-102	-172
XXI	427	220	200	207	195	- 92	-186
IX	417	-267	-260	- 80	- 79	-151	-161
XVIII	292	- 91	- 9	- 75	-106	-174	-162

5. THE SUBSIDIARY EXPERIMENT

The purpose of the subsidiary experiment was to obtain further information on certain phenomena that were observed in the course of the first experiment.

Among the phenomena that required confirmation or clarification were: (i) the decrease in growth and yield of rice in the well drained treatments as the availability of iron decreased; (ii) the better growth of rice under well drained than under submerged soil conditions during the early phase of growth; (iii) the retardation of the reduction process in the soil by nitrate; (iv) the remarkable recovery about heading time of the plants in the submerged, no-drainage treatments at the higher pH levels.

It was proposed to investigate these aspects of the main study on a limited scale but by more refined techniques.

5.1 Plan of the Experiment

The plan of the experiment envisaged growing rice on soils at three pH levels under the following conditions: (i) well drained, with and without added iron in the form of the relatively stable chelate FeNaEDTA*; (ii) well drained for the first thirty days of growth followed by submergence for the rest of the season; (iii) submerged continuously; (iv) submerged continuously but with nitrate added at the pH level at which accumulation of reduced substances was found to be most injurious to rice, and relatively large amounts of oat straw added at the higher pH levels at which the injurious effects of reduced substances was observed to be short-lived.

The fifteen treatments were studied in duplicate in a simple randomized block layout. Chemical and physicochemical analyses were made on the percolates from the submerged pots only while soil samples from all the pots were subjected to careful chemical analysis at frequent intervals. The physicochemical analyses were pH on percolates and soil samples, redox potential and conductance on the percolates. The chemical constituents analyzed were Fe, Mn, oxidizable matter, NH_4^+ , NO_3^- , and SO_4^{2-} on the percolates and Fe, Mn, K and P on Morgan extracts of the soil samples.

5.2 Materials and Methods

5.2.1 Materials

The soil used was, as before, a Mardin silt loam with a pH of 4.85. The two higher pH levels were obtained by treating this soil

* Ferric sodium ethylenediamine tetracetate.

with ground limestone at the rate of 3 1/4 and 4 1/4 tons per acre, respectively. The limed soils were kept in pots in a moist state in a field house during the month of April. Perhaps owing to the low temperature, the electrolyte content of the limed soils was not unduly high in contrast to the limed soils of the earlier experiment. Further the pH values of the limed soils (6.0 and 6.9) did not deviate appreciably from the planned values of 5.8 and 7.0 respectively.

5.22 Greenhouse Procedure

The soils at the three pH levels were given a basal dressing of 2,000 lbs. of a 5-10-5 mixture of ammonium sulfate, superphosphate and potassium chloride and placed in three gallon pots, 20 lbs. of soil to the pot. In the case of the oat straw treatments at pH 6.0 and 6.9, 0.5 percent oat straw was incorporated with the soil at the time of fertilization.

The iron treatment consisted of the addition of FeNaEDTA at a rate of 5 mg. of Fe per pot per day in the water added daily to keep the soils at field capacity. The relative instability of FeNaEDTA at high pH values, in soils, precluded the use of a single basal application.

The nitrate treatment consisted of the addition of 0.3 gm. nitrogen as sodium nitrate in the 3 liters of the water used for saturating the soil before submergence to a depth of 2".

The other treatments are self-explanatory.

The soils were moistened and six-week-old rice plants of the variety, Zenith, raised as before in sand culture, were planted at the rate of six plants per pot. The appropriate moisture treatments were then initiated.

The procedure for the collection of percolates and soil samples was exactly the same as before. The only modification was the determination of pH, conductance and redox potential in the percolates from the submerged pots at the instant they were drawn. For this purpose an electrometric cell, a diagrammatic sketch of which is given in Fig. 30, was used. The air was flushed out with nitrogen and the percolate allowed to flow by gravity into the cell. After the gas was completely displaced and about 10 c.c. of the percolate had run out, the inlet and outlet tubes were closed and the measurements made.

Conductance was measured with the conductivity bridge used before. pH and redox potentials were determined with a portable Beckman pH meter.

5.23 Chemical Procedures

The analytical procedures for the determination of Fe, Mn, oxidizable matter, NO_3^- , NH_4^+ and P were the same as before. The only new determinations were sulfate in the percolates and potassium in the Morgan extracts of the soils.

Sulfate was determined in the clarified percolates (zinc chloride, instead of zinc sulfate was used for the clarification) volumetrically by back titration of added barium chloride with disodium dihydrogen ethylenediamine tetracetate, in the presence of magnesium chloride, with Eriochromeschwarz T as indicator, as proposed by Munger et alia.*

Potassium was determined in the Morgan extracts with lithium as internal standard, in a Perkin-Elmer Flame photometer.

5.3 Results and Discussion

5.31 Physicochemical Analyses

The pH values of the percolates from each of the submerged pots on the several sampling dates are given in Table 20 of the Appendix while the pH values of the soil samples are given with other analytical figures in Tables 30-33 of the Appendix.

The general trend of the changes in pH both for the percolates and for the soils is very similar to that observed in the first experiment: the increase of the submerged soils was most marked at pH 4.9 and only a few tenths of a pH unit in the pH 6.9 treatments. Additional points of interest brought out in the second experiment are: (i) the pH value is higher in the percolate than in the soil sample at the pH 4.9 and the reverse at the two higher pH levels; (ii) the pH value of the soil of the nitrate treatment was consistently lower, especially in the early part of the season than that of the treatment without nitrate; (iii) the pH value of the soil of the oat-straw treatments was slightly lower than those of the soils of the no-oat-straw treatments during the early stages of the experiment.

The depressing effect of nitrate on the pH, despite the formation of sodium bicarbonate during denitrification, is due to the retardation of reduction. The decrease in pH in the oat-straw treatments may be attributed to the production of CO_2 and organic acids.

The conductance measurements (Table 21 of Appendix) indicate that the limed soils had, as in the previous experiment, a higher electrolyte content than the unlimed soils but the difference was not excessive. For this reason there was not the same sharp decrease in conductance in the early stages of submergence. The higher conductance of the

* Munger, J. R., Nippler, R. W. and Ingols, R. S. Volumetric determination of sulfate ion. Anal. Chem. 22: 1455-1457. 1950.

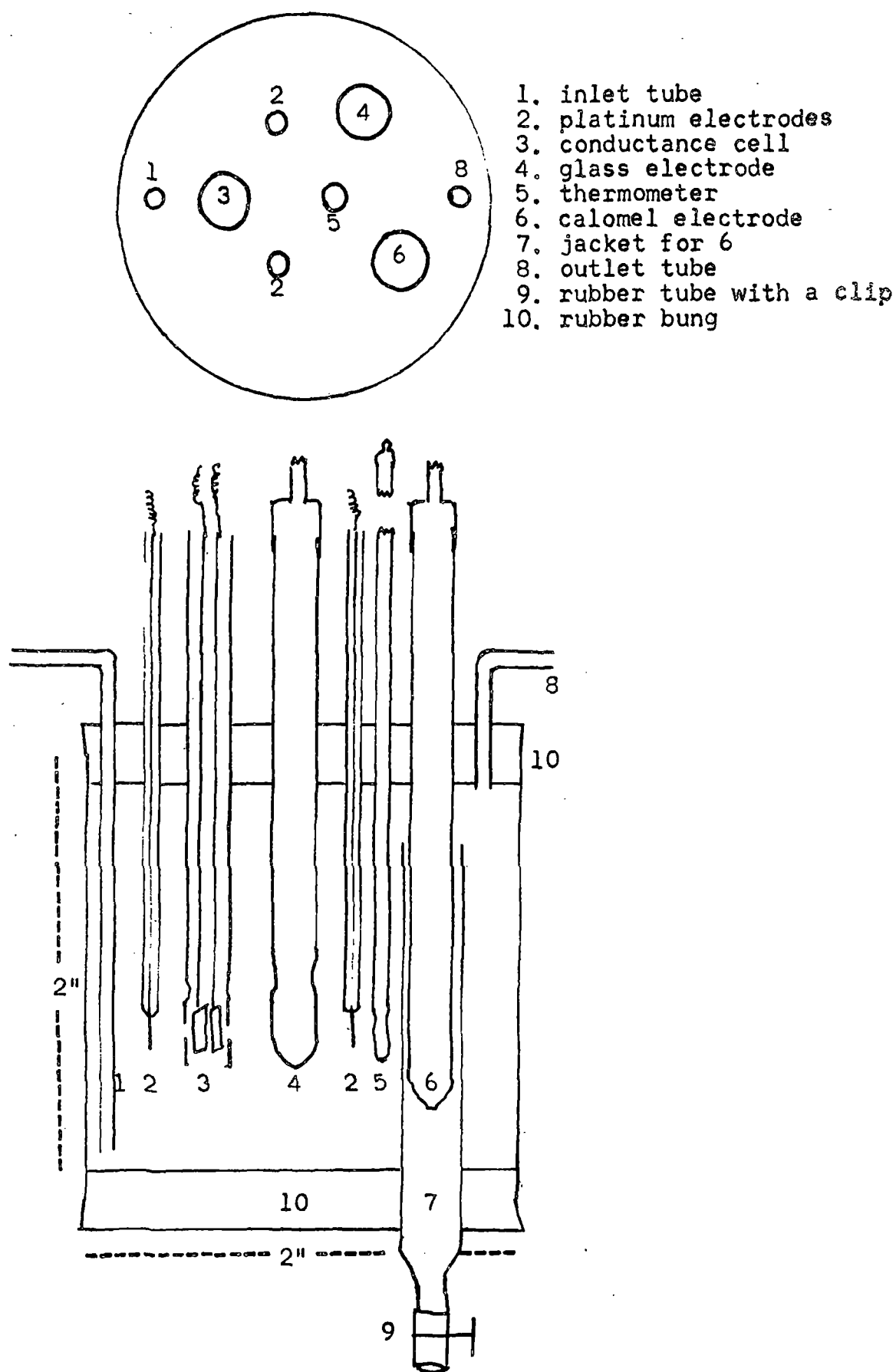


Fig. 30. Diagrammatic sketch of electrometric cell.

oat-straw treatments than the no-oat-straw treatments is no doubt associated with the higher concentration of iron and manganese.

The results of the redox potential determinations are given in Table 22 of the Appendix. The figures show that the potentials of the nitrate and no-oat-straw treatments are higher than those of the no-nitrate and oat-straw treatments respectively. But the differences are not as marked as they were among similar treatments in the previous experiment when potentials of the soil were measured in situ.

Some of the potential changes are represented graphically in Figure 31. The curves bring out some striking differences between potentials measured by the two methods. First, the decline in potential is less gradual for the soils at pH 4.9 and rather more rapid for the soils at pH 6.9 than in corresponding treatments in the earlier experiment. Secondly, the sharp minimum noted previously in the pH 4.9 treatment on the third day is absent. Thirdly, the potentials generally are higher than were observed with similar treatments in the earlier experiment. The lower potentials shown by the percolates is brought out clearly by the following figures for two highly reduced soils:

Pot No.	E_h in mv. 76 days after submergence	
	in situ	in percolate
30	-361	-37
8	-322	-29

That the higher potential of percolate is not due to contact with oxygen initially present in the cell is shown by the constancy of the potential in successive fillings of the electrometric cell.

Filling No.	E_h in mv. in percolate from pot no. 8 76 days from submergence
1	-29
2	-28
3	-30
4	-25
5	-27

The very much lower potentials in situ are probably due to the catalytic effect of enzymes, bacterial cells and the inorganic colloids in the soils -- an effect to which Michaelis (156) and also Puri and Sarup (190) had drawn attention to.

It may be concluded that redox potential of the soil measured in situ is an incomparably better index of the intensity of reduction of a soil than the redox potential of the percolate.

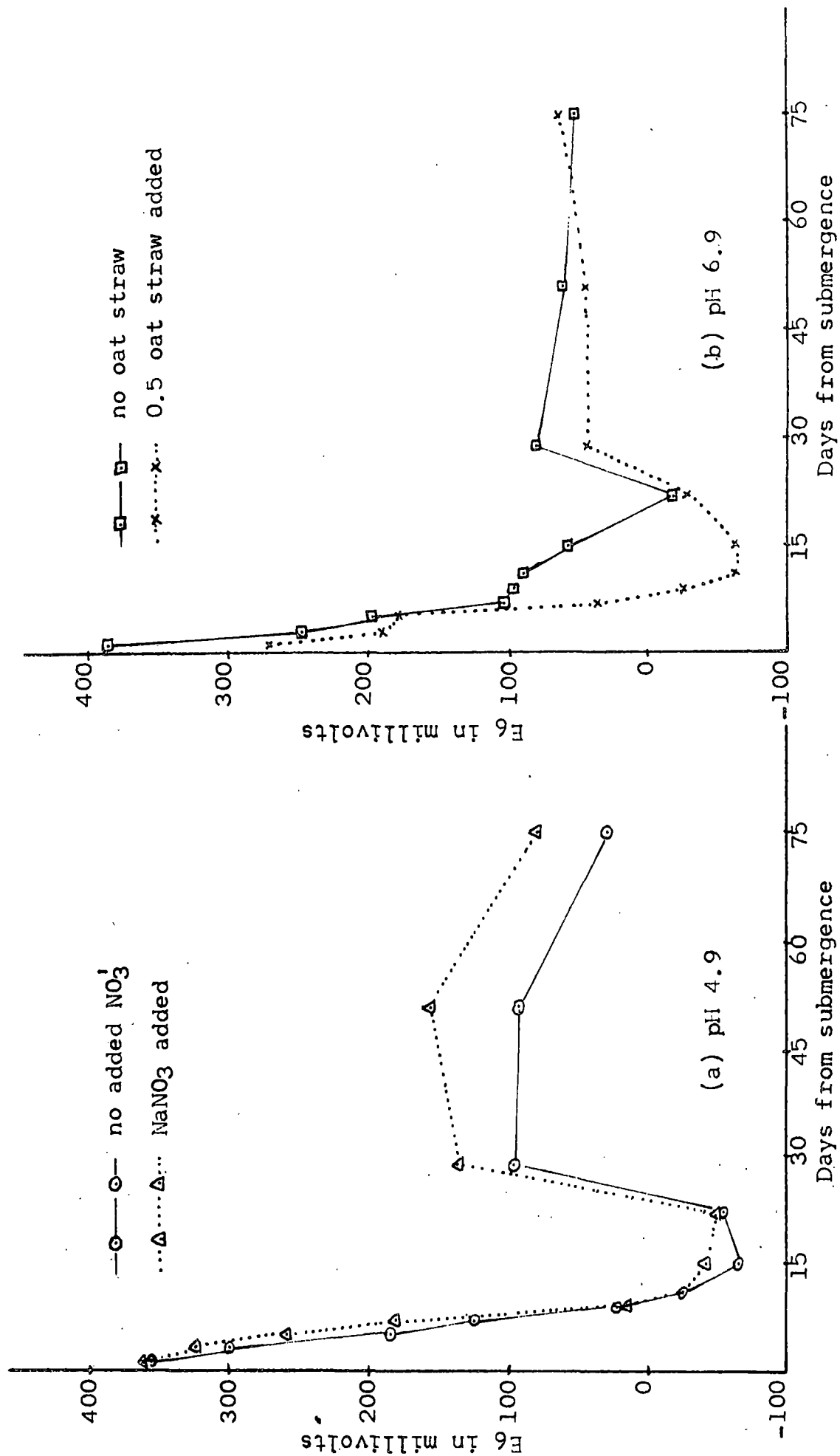


Fig. 31. Changes in redox potentials in percolates during period of growth.

Some typical physicochemical changes along with the associated chemical changes are represented in Figures 32 and 33.

5.32 Chemical Analyses

The detailed results of the chemical analyses are given in Tables 23-34 of the Appendix. It is proposed to discuss these results briefly under the appropriate heads.

(a) Analyses of Percolates

Iron. The mean values for the iron analysis for the submerged treatments, on each of the sampling dates, are assembled in Table 16.

The results reflect to a marked degree the treatment effects, especially in the early stages of submergence. As anticipated, the addition of nitrate has considerably retarded the accumulation of iron in the pH 4.9, continuously submerged treatment. The nitrate, however, was so rapidly used up during the first two weeks (the nitrate concentration was reduced from 84 p.p.m. N to less than 0.1 p.p.m. N) that at the sampling 22 days from submergence the iron concentration was comparatively high. At this stage 0.2 gm. N as sodium nitrate was added per pot. This caused a marked decrease in iron concentration as the value for iron on June 6 in Table 16, and also Figure 34 indicates. Apparently, nitrate not only retards reduction but also raises the level of oxidation-reduction. It is interesting to note that redox potential of the nitrate treatment after this addition of nitrate was considerably higher than that of the no-nitrate treatment and that Aoki (15) reported an increase in the redox potential of a submerged soil on the addition of nitrate. A further and final addition of 0.2 gm. N as sodium nitrate per pot was made on June 26. This evidently had a marked effect on the iron concentration at the following sampling about four weeks later for the nitrate treatment had only 78.5 p.p.m. iron in the percolate compared with the 328 p.p.m. in the no-nitrate treatment. But with the exhaustion of the nitrate supply the iron concentration began to climb steeply as Figure 34 indicates. The observation made in the earlier experiment that a submerged soil without drainage at a low initial pH could build up an astonishingly high concentration of soluble iron has been abundantly confirmed.

The no-oat-straw and oat-straw treatments at pH 6.0 and 6.9 follow, in the early stages the expected pattern: the iron concentration is higher in the presence of oat straw than in its absence and lower at the higher pH than at the lower pH. But the course of changes in iron concentration in the later stages is remarkably different from that observed in the earlier experiment.

It will be recalled that the iron concentrations of 0.4 percent oat-straw treatments at pH 5.7 and 6.0 rose steeply during the first 34 days of submergence and levelled off or showed a slight tendency to decrease while the no-oat-straw treatments showed a slow increase in the

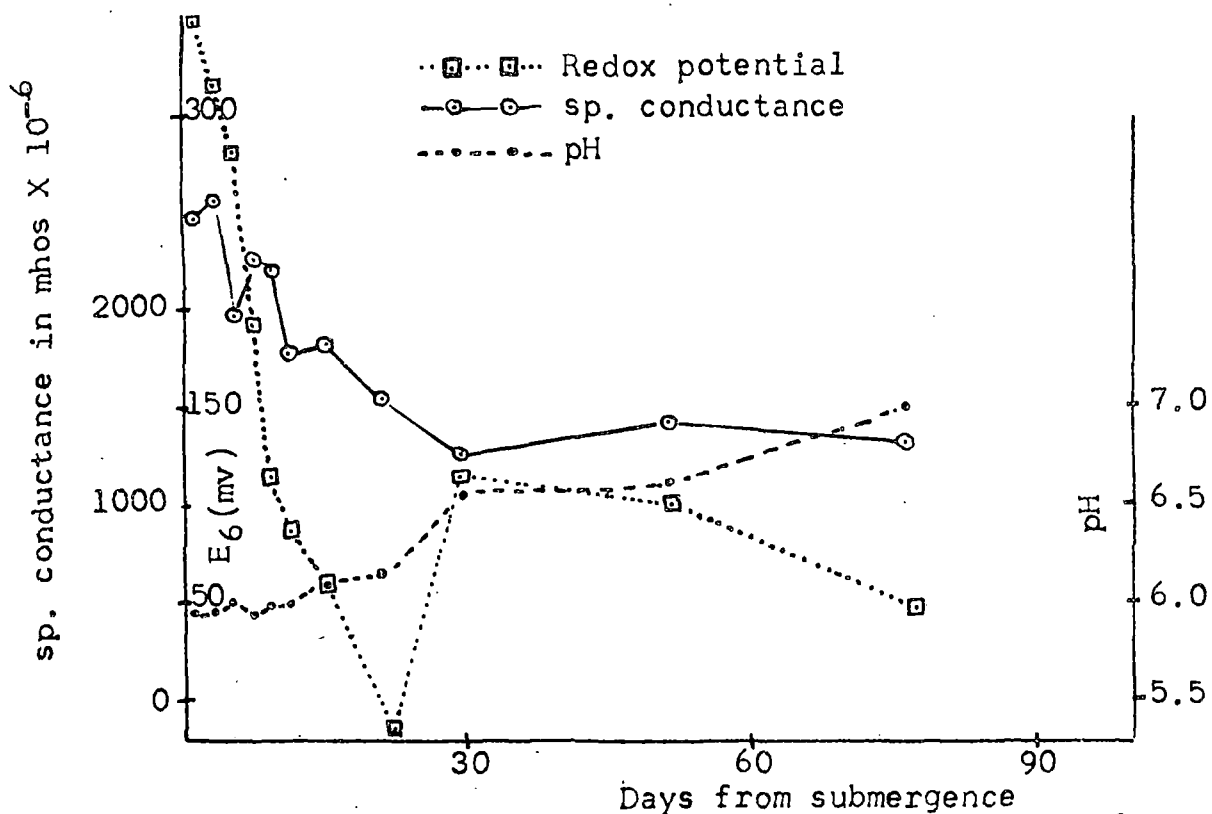


Fig. 32. Physico-chemical changes in percolates from pH 6.0 continuously submerged treatment.

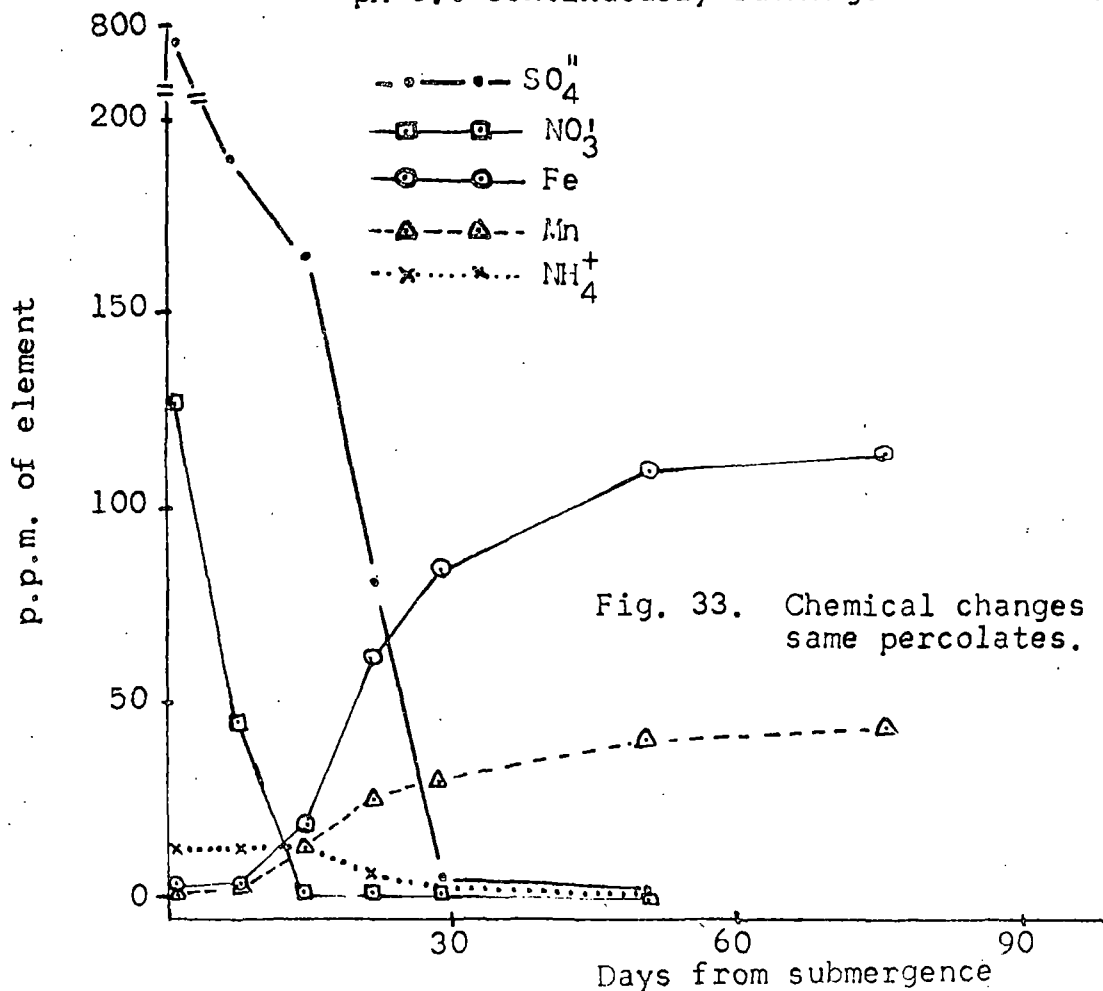


Fig. 33. Chemical changes in the same percolates.

TABLE 17
CHANGES IN CONCENTRATION OF Fe IN PERCOLATES DURING THE GROWING SEASON

Treat- ment No.	Treatment	Fe in p.p.m. of Percolate on						
		6/1*	6/8	6/15	6/22	6/29	7/21	8/14
3	pH 4.9 submerged on 6/30	-	-	-	-	2.7	82.0	282
4	pH 4.9 submerged continuously	1.3	10.7	62.3	83.0	80.0	328	368
5	pH 4.9 sub. cont. NaNO_3 added	0.8	6.6	34.5	71.0	6.4	78.5	428
8	pH 6.0 submerged on 6/30	-	-	-	-	1.2	55.5	106
9	pH 6.0 submerged continuously	2.0	3.4	18.9	60.3	83.5	109	114
10	pH 6.0 sub. cont. 0.5% oat straw added	2.5	43.4	127	212	248	89	34.0
13	pH 6.9 submerged on 6/30	-	-	-	-	0.8	38.5	47.0
14	pH 6.9 submerged continuously	0.5	5.7	14.3	46.8	48.0	69.5	51.5
15	pH 6.9 submerged continuously 0.5% oat straw added	3.1	33.6	63.5	124	143	63.5	33.5

* One day after transplanting and submergence.

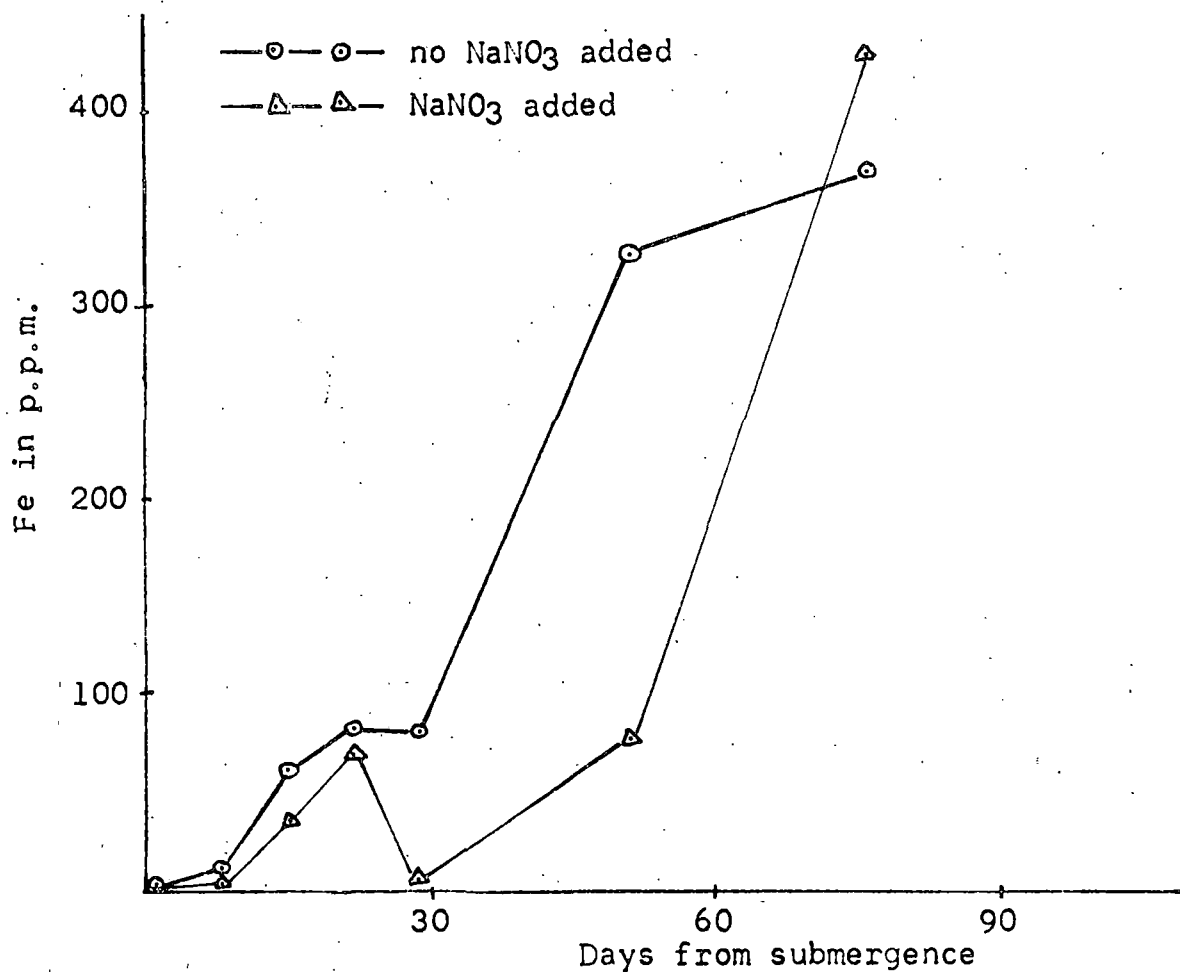


Fig. 34. Changes in conc. of Fe in percolates, pH 4.9 treatment.

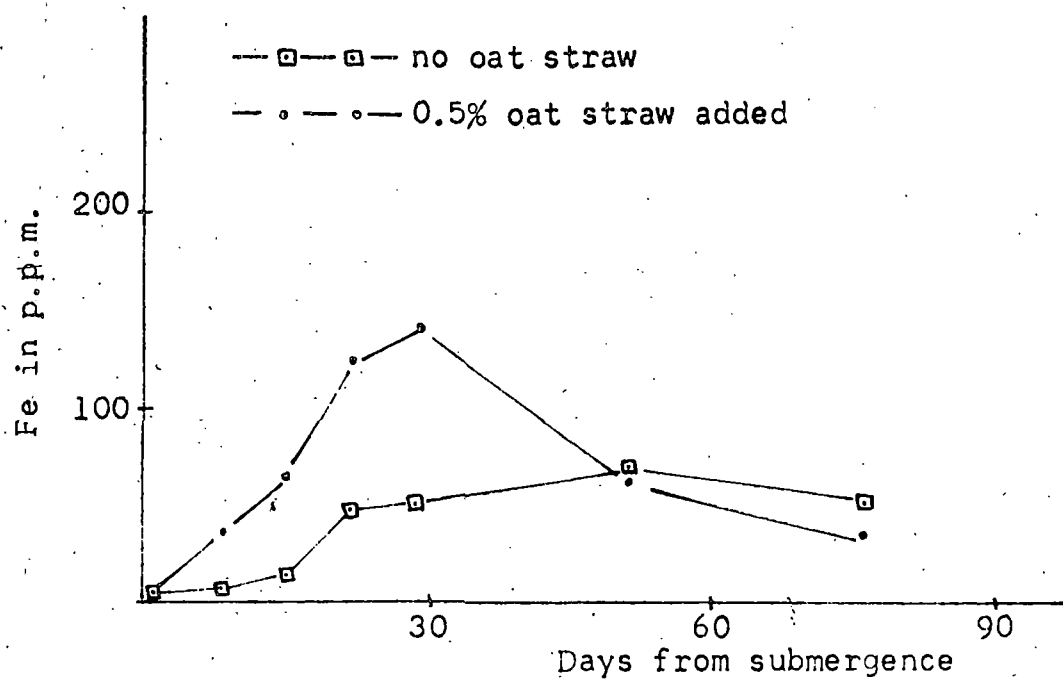


Fig. 35. Changes in concentration of Fe in percolates, pH 6.9 treatment.

early stages but an accelerated increase in the later stages. In the present experiment the tendency of iron concentrations in the oat-straw treatments to decrease in the later stages has been markedly accentuated while the trend towards higher iron concentration at this time in the no-oat-straw treatments has been arrested. The explanation of this behavior with the available information can only be speculative.

The accentuation of the decrease in water-soluble iron at the two high pH values, in the later stages, in this experiment is probably associated with climatic factors far more favorable to the rice plants and to certain biochemical changes in the soil.

In the experiment rice seedlings were transplanted on June 1 and grew under the favorable climatic conditions of a warm, bright summer while in the earlier experiment the seedlings were transplanted on August 1 and grew during a period of dwindling intensity and duration of light and decreasing temperature. The plants of the second experiment thus grew better and had more vigor than those of the earlier experiment. Perhaps the larger amount of oxygen exuded by the more vigorous plants assisted the removal of iron from solution. According to Van Raalte (193) the oxidizing capacity of a two-month-old rice plant is equivalent to 1-3 mgm oxygen, per day. Assuming the low value of 1 mgm per plant per day it can be shown that about 8 percent of the iron reduced during the first 11 weeks, is reoxidized to the ferric state. Now Arden (16) has shown that ferric hydroxide iron tends to form mixed hydroxides with ferrous hydroxide whose solubility products are much lower than for pure ferrous hydroxide especially if a little oxygen is present. The lowering of the solubility product of ferrous hydroxide may be one of the factors responsible for the decrease in concentration of soluble iron.

The other factor is probably the more rapid transformation of organic acids formed during the anaerobic decomposition of organic matter, into gases in the temperature range, 30-35°, than below this range (2). It may be mentioned that temperatures as high as 32° C were recorded in the percolates as they were drawn into the electrometric cell and that in the later stages considerable difficulty was experienced in the collection of the percolates owing to retardation of flow by gas bubbles in the outlet tubes from the pots. With the destruction of the organic acids the concentration of iron presumably reverted to the levels permitted by ionic equilibria.

The results of this experiment: (i) confirm the retardation of reduction of iron by nitrate; (ii) suggest that the rice roots exert an appreciable oxidizing influence on their environment; (iii) climatic factors influence the concentration of soluble iron.

Manganese. The detailed results of the manganese analyses are given in Tables 23-29 of the Appendix. The general pattern of changes in manganese concentrations is similar to that of iron so that a detailed discussion of these results is unnecessary. The interesting feature of the Fe:Mn ratio, to which reference was made in the first experiment, however, merits some comment.

The changes in the Fe:Mn ratio in the percolates during the growing season are given in Table 17. In treatment no. 4, where reduction proceeded uninterrupted, there is a steady increase in the ratio. The lower state of reduction of the nitrate treatment in the early stages is reflected in the much lower Fe:Mn ratio. The oxidizing conditions brought about by the addition of nitrate on June 26, to which reference was made in the discussion of the iron results is reflected in the decline of the ratio from 2.60 on June 22 to 0.58 on June 29. The increase in reduction following the exhaustion of nitrate is accompanied by a sharp increase in the ratio.

At the two higher pH values the ratio for the first sampling date is erratic and reflects the errors in the determination of very small amounts of the two elements. The subsequent course of the Fe:Mn ratio follows generally the reduction pattern. It is higher in the oat-straw treatment than in the no-oat-straw treatment on practically all sampling dates. Further, it increases as the reduction proceeds and decreases in the later stages when the concentration of reduced products diminishes.

It would appear that the Fe:Mn ratio is a fair index of the degree of reduction of submerged soils of comparable pH.

Oxidizable matter. The figures for oxidizable matter are given with the other analyses in Tables 23-29 of the Appendix. In general the values for oxidizable matter are roughly parallel to those of iron and manganese.

Nitrate and ammonium. The general trends of these analyses (Tables 23-29 of Appendix) are very similar to those observed in the first experiment. As before, nitrate rapidly disappeared, while ammonium increased in the oat-straw treatments, during the first three weeks of submergence. The increase of ammonium in the percolates was no doubt due to the displacement of NH_4^+ from the soil colloids by the Fe^{+2} and Mn^{+2} that were formed in large amounts in these treatments in the early stages. The marked decline of ammonium in all but the oat-straw treatments during the third week of June coincides with the extremely rapid growth of the plants. Chlorosis of the older leaves was apparent when the ammonium concentration in the percolate was down to about 2 p.p.m. All pots were therefore given a dressing of ammonium sulfate at the rate of 100 lbs. per acre on July 21, i.e., 7 weeks from transplanting.

Sulfate. The results of the sulfate analysis during the season indicate: (i) a rapid reduction of sulfate in the oat-straw treatments; (ii) the somewhat greater stability of SO_4 than NO_3 ; (iii) the retardation of the reduction of sulfate by the presence of nitrate.

The disappearance of sulfate has little ecological significance because: (i) rice plants absorb most of their sulfur requirements in the early stages of growth before reducing conditions become intense enough to cause the disappearance of sulfate; (ii) the oxidized environment of the rice roots ensures an adequacy of sulfate from the oxidation of FeS.

TABLE 18

INFLUENCE OF THE DEGREE OF REDUCTION ON THE Fe:Mn RATIO DURING THE GROWING SEASON

Treatment No.	Treatment	Fe:Mn Ratio in Percolates on						
		6/1*	6/8	6/15	6/22	6/29	7/21	8/14
4	pH 4.9 submerged continuously	0.42	0.53	2.05	3.26	3.77	4.75	4.24
5	pH 4.9 sub. cont. NaNO_3 added	0.20	0.49	1.33	2.60	0.58	2.19	5.79
9	pH 6.0 submerged continuously	2.22	1.03	1.42	2.34	2.82	2.67	2.55
10	pH 6.0 sub. cont. 0.5 per cent oat straw added	1.46	1.56	2.72	4.08	4.39	2.70	2.20
14	pH 6.9 submerged continuously	0.83	3.16	1.86	2.31	1.85	1.86	2.22
15	pH 6.9 sub. cont. 0.5 per cent oat straw added	3.89	2.51	2.00	3.18	3.28	2.19	2.70

* One day after transplanting and submergence.

(b) Analyses of Soil Samples

The analyses of Morgan extracts of the soils samples taken at intervals during the growing season are given in Tables 30-34 of the Appendix. The analyses of the more important constituents will be discussed below.

Iron. The mean analyses of iron for the 15 treatments are given in Table 19. They reflect to a marked degree, though at different stages, the treatment effects.

The well drained soils are characterized by concentrations of iron which are low and which vary little with time. Among these soils the figures for iron decrease with increase in pH level. There is no appreciable difference between the FeNaEDTA treatments and the no FeNaEDTA treatments till the fourth sampling (i.e. 51 days from start). After this date the effect of the FeNaEDTA additions is reflected in the higher figures for iron extractable in Morgan's reagent.

The treatments in which submergence was delayed for 30 days show the expected high figure for iron after submergence.

Other points of interest are the lower content of iron in the early stages in the nitrate treatment, the marked increase of iron in the oat-straw treatments, and the tendency of the iron figures for the submerged treatments to approach a common level. It may also be noted that although water soluble iron decreased in the submerged treatments at pH 6.0 and 6.9, though not at pH 4.9, iron extractable in Morgan's solution progressively increased. Presumably Morgan's solution at pH 4.8 with its high buffer capacity extracts the mixed ferrous and ferric hydroxides which according to Arden (16) separate out at pH 5.3.

Manganese. The mean values of the manganese analyses for the 15 treatments are given in Table 20.

The changes in manganese concentrations of Morgan extracts of the soils were discussed in detail under the earlier experiment. No new facts have been brought to light. It may, however, be emphasized that manganese in the well drained soils far from following the iron pattern of decreasing with increasing pH is in fact highest at the highest pH level. Also the previous observation that manganese extractable in Morgan's reagent in the submerged soils tends to a common level, irrespective of pH and oat-straw treatments, has been confirmed.

Phosphorus. The detailed phosphate analyses are given in Tables 30-34 of the Appendix while the mean values are represented in Table 21.

The analyses for the first two sampling dates do not appear to follow any treatment pattern. But from the third week onwards the submerged treatments all show a steady increase in phosphorus extractable in Morgan's solution while the well drained treatments (Fig. 37) show fluctuations which may be associated with sampling errors. The increase

TABLE 19
CHANGES IN CONCENTRATION OF IRON IN MORGAN EXTRACTS DURING THE GROWING SEASON

Treatment No.	Treatment	Days from Start				
		0	8	23	51	76
		Fe in lbs. per acre				
1	pH 4.9, well drained	32.0	39.6	28.2	30.8	39.8
2	pH 4.9, well drained, Fe added	33.9	44.3	31.9	46.7	52.5
3	pH 4.9, submerged on 6/30	31.4	43.5	30.1	2390	5375
4	pH 4.9, submerged from start	30.9	100	2630	5165	6440
5	pH 4.9, sub. from start, NaNO_3 added	31.7	53.8	578	4995	6190
6	pH 6.0, well drained	19.3	34.1	18.3	19.4	19.1
7	pH 6.0, well drained, Fe added	19.4	35.6	22.9	37.8	60.3
8	pH 6.0, submerged on 6/30	18.5	32.2	15.4	3330	5425
9	pH 6.0, submerged from start	18.3	54.0	3085	6285	6125
10	pH 6.0, sub. from start 0.5% oat straw added	17.5	810	4160	6340	7165
11	pH 7.0, well drained	12.9	32.4	14.9	24.5	15.7
12	pH 7.0, well drained, Fe added	14.0	30.8	18.7	51.6	37.7
13	pH 7.0, submerged on 6/30	13.2	31.3	16.7	2830	5885
14	pH 7.0, submerged from start	14.9	106	3510	5880	6910
15	pH 7.0, submerged from start 0.5% oat straw added	14.4	1778	4295	7365	7520

TABLE 20

CHANGES IN CONCENTRATION OF MANGANESE IN MORGAN EXTRACTS DURING THE GROWING SEASON

Treatment	Days from Start					
	0	8	Mn in lbs. per acre	23	51	76
1. pH 4.9, well drained	45.0	40.6	30.0	31.1	29.4	
2. pH 4.9, well drained, Fe added	46.0	39.3	31.6	25.9	34.8	
3. pH 4.9, submerged on 6/30	50.0	39.4	38.0	378	414	
4. pH 4.9, submerged from start	47.5	214	382	461	439	
5. pH 4.9, submerged from start NaNO ₃ added	46.0	159	309	392	450	
6. pH 6.0, well drained	35.0	41.9	33.0	19.3	26.4	
7. pH 6.0, well drained, Fe added	35.0	36.7	31.8	22.0	34.2	
8. pH 6.0, submerged on 6/30	33.0	33.6	24.8	380	336	
9. pH 6.0, submerged from start	36.5	130	389	444	398	
10. pH 6.0, submerged from start 0.5% oat straw added	37.0	326	396	450	357	
11. pH 7.0, well drained	49.0	56.3	-	48.2	49.8	
12. pH 7.0, well drained, Fe added	39.5	52.0	36.3	45.9	63.0	
13. pH 7.0, submerged on 6/30	43.0	50.2	38.0	385	401	
14. pH 7.0, submerged from start	48.0	206	389	427	369	
15. pH 7.0, submerged from start 0.5% oat straw added	46.0	397	383	473	484	

in the content of soluble phosphate with time suggested that it may be a consequence of the reduction process. The association between the reduction process (as measured by the amount of iron extractable in Morgan's reagent) and the increase in solubility of phosphate is shown qualitatively in Fig. 36. The rough parallelism between iron and phosphorus extractable in Morgan's reagent is apparent.

A closer examination of the iron and phosphorus figures for the submerged soils from the third week onwards suggested that the relationship was clear enough to be described quantitatively. A second degree polynomial was therefore fitted to these figures and a highly significant correlation obtained. The relationship between phosphorus and iron may be described by the expression:

$$Y = 6.4 + 1.3 \times 10^{-5}X + 14.0 \times 10^{-8}X^2$$

where X and Y are the amounts of iron and phosphorus respectively (extractable in Morgan's reagent) in any one of the submerged treatments, after 23 days from start of the experiment. A graphic representation is given in Figure 38.

It may, however, be objected that the apparent increase in soluble phosphorus following submergence, observed by numerous investigators, and confirmed in this study, may be a reflection of a systematic analytical error, for both iron and silica cause interferences in the methods of phosphate analysis. Although these errors are reduced to a minimum in Martin and Doty's (152) isobutanol-benzene extraction procedure it was felt that the interferences merited investigation.

The study indicated that iron (as ferrous acetate) even at 500 p.p.m. caused no interference but silica introduced a positive error which increased progressively from 6 percent at 10 p.p.m. Si (as sodium metasilicate) to 16 percent at 50 p.p.m. Si. The silica contents of some of the Morgan extracts analyzed were of the order of 15 p.p.m. Si for submerged soils and a few parts p.p.m. less for the well drained soils. Incidentally, the slight error due to silica may be eliminated by using a smaller volume of Morgan extract and a slightly higher concentration of acid in the molybdate reagent.

The increases in soluble phosphorus contents in the submerged soils are so much higher than the possible error that there is little doubt about their reality.

Potassium. The detailed potassium analyses are given in Tables 30-34 of the Appendix.

The figures show: (i) a high level of potassium in the oat-straw treatments throughout the season; (ii) a lower level of potassium in the submerged than in the well drained treatments after the first 23 days of growth of rice plants.

TABLE 21

CHANGES IN CONCENTRATIONS OF PHOSPHORUS IN MORGAN EXTRACTS DURING THE GROWING SEASON

Treatment No.	Treatment	Days from Start				P in lbs. per acre	
		0	8	23	51		
1	pH 4.9, well drained	8.8	10.9	6.5	8.6	6.1	
2	pH 4.9, well drained, Fe added	9.1	10.2	6.8	6.3	5.6	
3	pH 4.9, submerged on 6/30	9.6	10.9	7.4	7.9	11.9	
4	pH 4.9, submerged from start	8.7	9.6	7.7	11.9	13.5	
5	pH 4.9, submerged from start NaNO ₃ added	8.9	9.4	7.2	9.2	13.9	
6	pH 6.0, well drained	8.3	7.7	5.3	5.4	5.6	
7	pH 6.0, well drained, Fe added	8.2	7.7	5.1	5.8	5.0	
8	pH 6.0, submerged on 6/30	7.4	8.5	5.6	8.2	10.1	
9	pH 6.0, submerged from start	8.4	7.5	7.3	11.5	13.6	
10	pH 6.0, submerged from start 0.5% oat straw added	9.7	10.0	10.9	14.1	13.5	
11	pH 7.0, well drained	9.4	6.7	4.7	5.0	5.8	
12	pH 7.0, well drained, Fe added	8.3	8.4	4.7	6.3	5.5	
13	pH 7.0, submerged on 6/30	12.4	8.0	6.6	7.2	11.6	
14	pH 7.0, submerged from start	10.1	6.0	8.2	10.8	13.0	
15	pH 7.0, submerged 0.5% oat straw added	12.5	9.3	10.0	16.0	15.8	

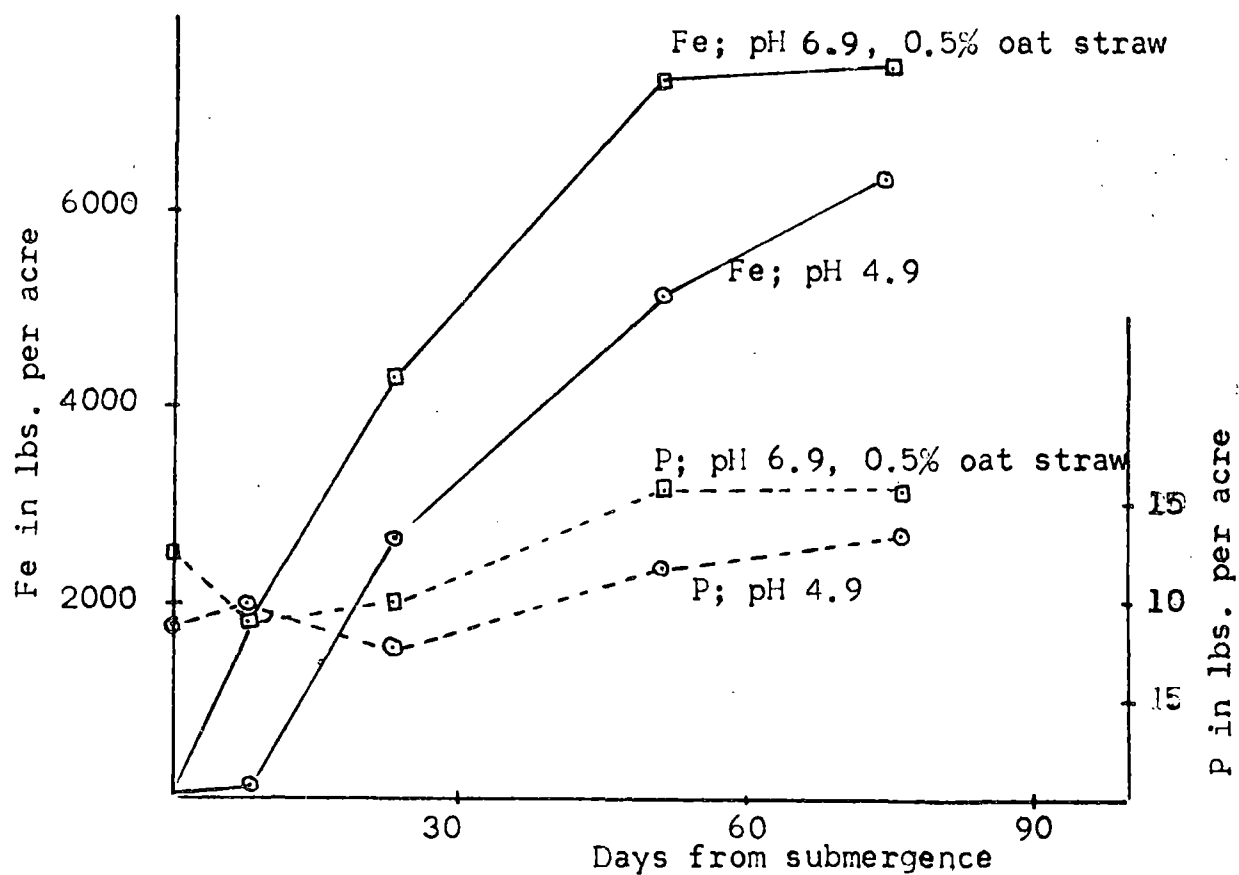


Fig.36. Changes in content of Fe and P soluble in Morgan's solution of two submerged soils.

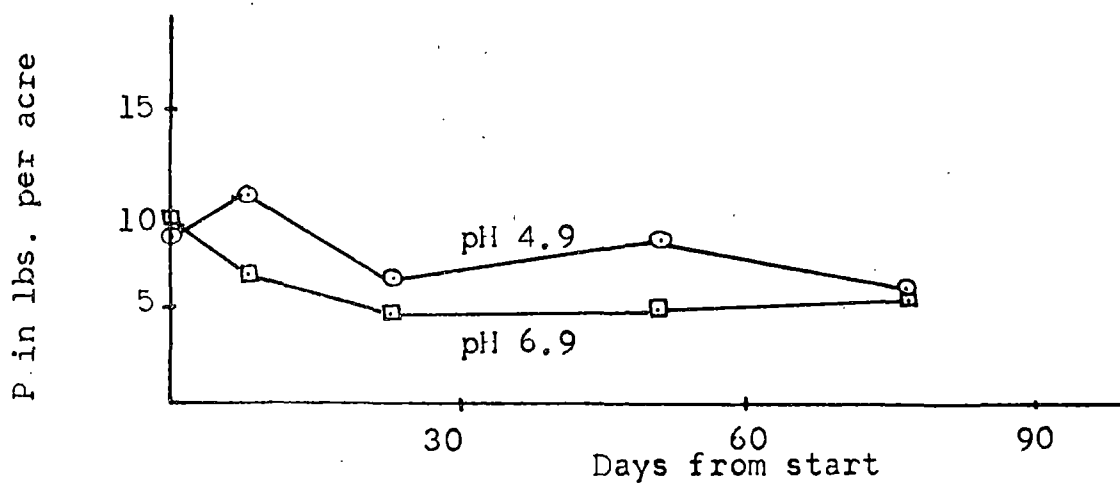


Fig. 37. Changes in content of P soluble in Morgan's solution of corresponding well drained soils.

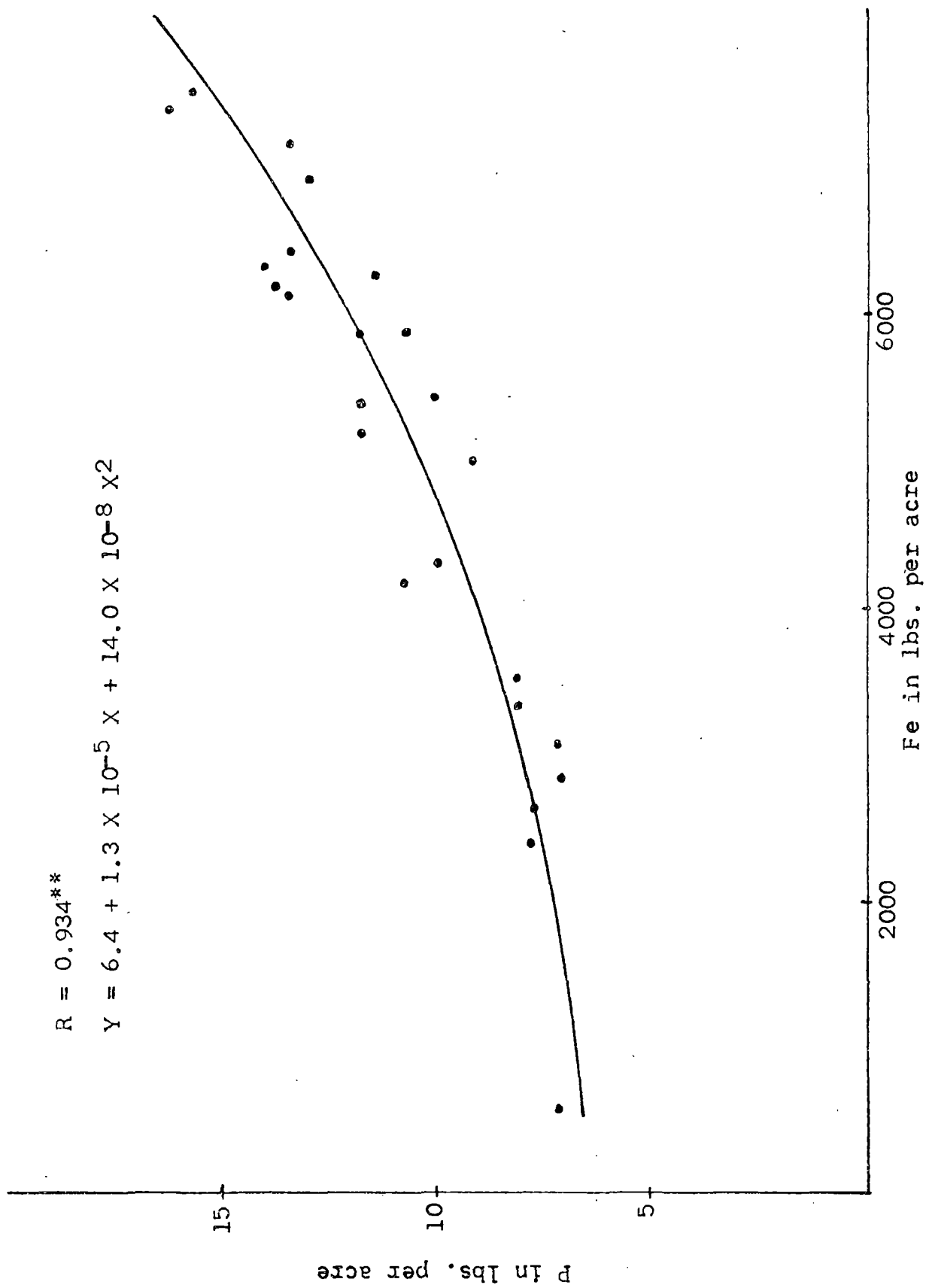


Fig. 38. Relationship between phosphate and iron in Morgan extracts of submerged soils.

The high level of potassium in the oat-straw treatments reflects the additional (approximately) 100 lbs. per acre of potassium conveyed in the oat straw. The lower figures in the submerged treatments were at first not intelligible. The possibility of analytical errors was therefore investigated. Since the Morgan extracts on which potassium was run had high concentrations of iron and manganese, interference by these two elements was examined. The results revealed that iron at even 500 p.p.m. and manganese at 50 p.p.m. alone or in combination caused no interference in the determination of potassium by the internal standard method, flamephotometrically. The lower potassium figures for the submerged soils was probably due to the greater assimilation associated with the better growth of the plants in the submerged than in the well drained treatments.

5.33 Growth and Yield Data

5.331 Growth Characteristics

The six-week-old rice seedlings which had been raised, as before, in submerged sand culture containing Hoagland solution fortified with 10 p.p.m. Fe as FeNaEDTA were transplanted on June 1.

No marked differences were noticed among the treatments until about two weeks after transplanting. At this stage the most striking feature was the marked superiority of the well drained treatments to the submerged ones. Among the well drained treatments there were no noticeable differences but treatment effects were clearly manifest in the submerged treatments. The pH 4.9, submerged nitrate-treatment was by far the best and the submerged oat-straw treatments by far the worst. The submerged oat-straw treatments were considerably retarded in growth, showed signs of incipient wilting during the heat of the afternoon and were the only treatments in which guttation, in the early part of the morning, was not noticeable. Apparently, excess CO_2 and other products of the anaerobic decomposition of the oat straw had reduced appreciably water and nutrient uptake.

Four weeks from transplanting the over-all situation was very much the same: the well drained treatments were still better than the submerged ones and among these the oat-straw treatments were still the worst, and the nitrate ones, the best. But certain changes were noticeable. The well drained treatments were dark green in color while all the submerged treatments, except the nitrate treatment, were somewhat pale green in color. Among the well drained treatments the only noticeable difference was the drooping of the laminae of the pH 6.0 and pH 6.9 plants. Among the submerged treatments, the nitrate treatment stood out boldly by its luxuriant growth, its dark green color, and profuse tillering. The no-nitrate treatment at the same pH, in contrast, looked poor by all standards. The oat-straw treatments which had suffered a severe setback were now beginning to recover.

Thirty days after transplanting a well drained treatment at each pH level was submerged to a depth of 2" and the level maintained by daily additions of distilled water.

A week later, clear responses to flooding were apparent. The tillers which had all been compressed together now spread out fanwise. This was no doubt due to the removal of mechanical hindrances to the lateral spread of tillers. The other remarkable feature was the presence of fine white roots at the surface of the soil. The development of these roots was probably a response to the sudden change of the root environment from aerobic to anaerobic. Fine white superficial roots, however, were observed in the nitrate treatment and to a lesser extent in the other submerged treatments. It will be recalled that the development of a mat of fine superficial roots is a normal event in the growth of rice under flooded conditions.

Yet another observation five weeks after transplanting was the pale green color of the submerged treatments with the exception of the nitrate, oat-straw, and the newly flooded treatments. The chemical analyses revealed that NH_4 was running low. A dressing of ammonium sulfate at the rate of 100 lbs. per acre was given to all treatments. A more remarkable observation was the presence of brown spots on the older leaves of the submerged pH 4.9 treatments. The submerged nitrate-treatment at the same pH level did not show a trace of this speckling.

Two weeks later, i.e., seven weeks from transplanting, many interesting differences were noted among the treatments. The well drained treatments were still better looking than the majority of the submerged ones but among them the iron treatments looked more vigorous and darker green than the no-iron treatments. The striking features of the submerged treatments were: (i) the marginal scorch of older leaves and the spread of the brown speckling to the younger leaves in the pH 4.9 treatment; (ii) the appearance of brown spots on the older leaves of the continuously submerged treatments at pH 6.0; (iii) the presence of a few faint brown spots even in the nitrate treatment at pH 4.9; (iv) the astonishing recovery of the submerged oat-straw treatment at pH 6.9.

Eight weeks from transplanting, marginal scorch and the reddish discoloration of leaf tips were pronounced in the submerged pH 4.9 treatment. Similar symptoms in a milder form were present in the pH 4.9-submerged-nitrate-treatment too. It is interesting to note that the symptoms began to appear in this treatment only after the nitrate supply was exhausted and large amounts of iron and manganese had begun to appear in the soil solution.

The next two weeks were marked by a lull in activity on the part of most treatments except the oat-straw treatments which continued to grow rapidly.

The eleventh week from transplanting marked the beginning of heading, accompanied by rapid culm elongation, in all the submerged

treatments though variations with treatments were noticeable. The remarkable feature at this stage was the dramatic growth of the late submergence treatments which up to this time had shown no marked response to the flooding. The iron treatments among the well drained soils also elongated and had a healthy appearance while the no-iron well drained treatments at pH 6.0 and 6.9 were languishing. Another interesting observation was the presence of brown spots and a slight marginal scorch on the late-submerged treatment at pH 4.9. The chemical analyses revealed the presence of approximately 250 p.p.m. iron in the percolates from this treatment. The iron figures for the no-nitrate and nitrate treatments at the same pH level, in which scorching of the older leaves was by now very severe, were approximately 400 p.p.m. ✓

The growth characteristics of all but one of the 15 treatments are presented graphically in Figures 39-41. The growth of the iron treatment at pH 4.9 is omitted because it is almost identical with that of the no-iron treatment. Plates IV and V show the differences among the no-iron, iron, and late submergence treatments at pH 4.9 and pH 6.9.

Blooming commenced about the middle of August and was spread over a period of two weeks. The last to bloom were the well drained, no-iron treatments at pH 6.0 and 6.9. These treatments like the similar treatments of the first experiment showed hardly any culm elongation at heading time. An additional feature of these two treatments was a slight intervenal chlorosis of the younger leaves.

All except the diseased pH 4.9 treatments and the well drained treatments at pH 6.0 and 6.9 produced normal panicles with no appreciable number of sterile florets. In the scorched plants of the pH 4.9 treatments and the plants of the well drained pH 6.0 and 6.9 treatments, particularly the no-iron treatments, the panicles were thin and narrow and had a fair proportion of sterile florets.

The observations on growth may be summarized as follows: (i) the no-iron well drained treatments made satisfactory growth during the first five weeks after transplanting and then suffered a retardation in growth which was most severe at the highest pH level; (ii) the well drained treatments with added iron, though similar in behavior to the no-iron treatments in the early stages, made rapid growth at the time of heading; (iii) late submergence markedly increased growth over the continuously well drained treatments; (iv) the submerged pH 4.9, nitrate-treatment was distinctly superior to the pH 4.9, submerged no-nitrate treatment; (v) brown spots, a reddish discoloration and leaf scorch were severe in the two pH 4.9, submerged treatments though nitrate considerably delayed the onset of the symptom; (vi) the submerged oat-straw treatments at pH 6.0 and 6.9 though considerably retarded at the start, later recovered and even excelled the no-oat-straw treatments.

5.332 Yield Figures

Growth and yield figures are given in detail in Table 35 of Appendix. The mean values for each treatment are given in Table 22. Only

the grain yields were analyzed statistically. A simple analysis of variance indicated that the treatment effects were highly significant. Differences among the treatments were tested for their significance by the Duncan multiple range test.

The growth and yield figures for the well drained treatments, with and without added iron, are represented graphically in Figure 42. It is clear that in all respects the pH 6.0 and 6.9 treatments are markedly inferior to the pH 4.9 treatment, but the pH 6.9 treatment is not appreciably different from the pH 6.0. There is a highly significant decrease in grain yield from pH 4.9 to 6.0. The decrease from pH 6.0 to 6.9 is not significant.

Figure 42 also brings out the effect of the daily addition of 5 mgm Fe as FeNaEDTA to the well drained treatments. Iron has increased the number of tillers, the height of plants, and the yield of both straw and grain, but only at pH 6.0 and 6.9. At a pH of 4.9 the addition of iron, though beneficial, has caused no appreciable improvement. The increases in grain yield over the no-iron treatments at both pH 6.0 and 6.9 are highly significant.

Figure 43 brings out the parallelism between the decrease in yield and decrease in iron extractable in Morgan's reagent, as pH increases. The iron values used are the mean analyses of the well drained no-iron treatments at the start of the experiment.

The effect of delaying submergence for 30 days varies. At pH 4.9 it has caused a significant increase in yield over the well drained treatments but a highly significant increase over the continuously submerged treatments, with and without the addition of nitrate. At pH 6.0 and 6.9 while the increase over the well drained treatments is highly significant, the contrast with the continuously submerged treatments is not significant.

The difference between the nitrate and no-nitrate continuously submerged treatments at pH 4.9 is limited to weight of straw and the number of tillers. It will be recalled that in the early stages of growth when the iron concentration was kept low by the presence of nitrate the plants tillered profusely and grew luxuriantly. With the exhaustion of the nitrate supply the iron concentration increased rapidly with the result that at about the time of heading these plants suffered presumably from iron toxicity as much as the plants of the no-nitrate treatment. Thus there is no significant difference in grain yield between these two treatments although the straw yield is 50 percent higher and the number of tillers 40 percent greater than in the no-nitrate treatments. It must be stated, however, that the pots of the nitrate treatment, probably because of their dense foliage, were repeatedly attacked by rats. The grain yield had therefore to be computed from the small number of undamaged panicles.

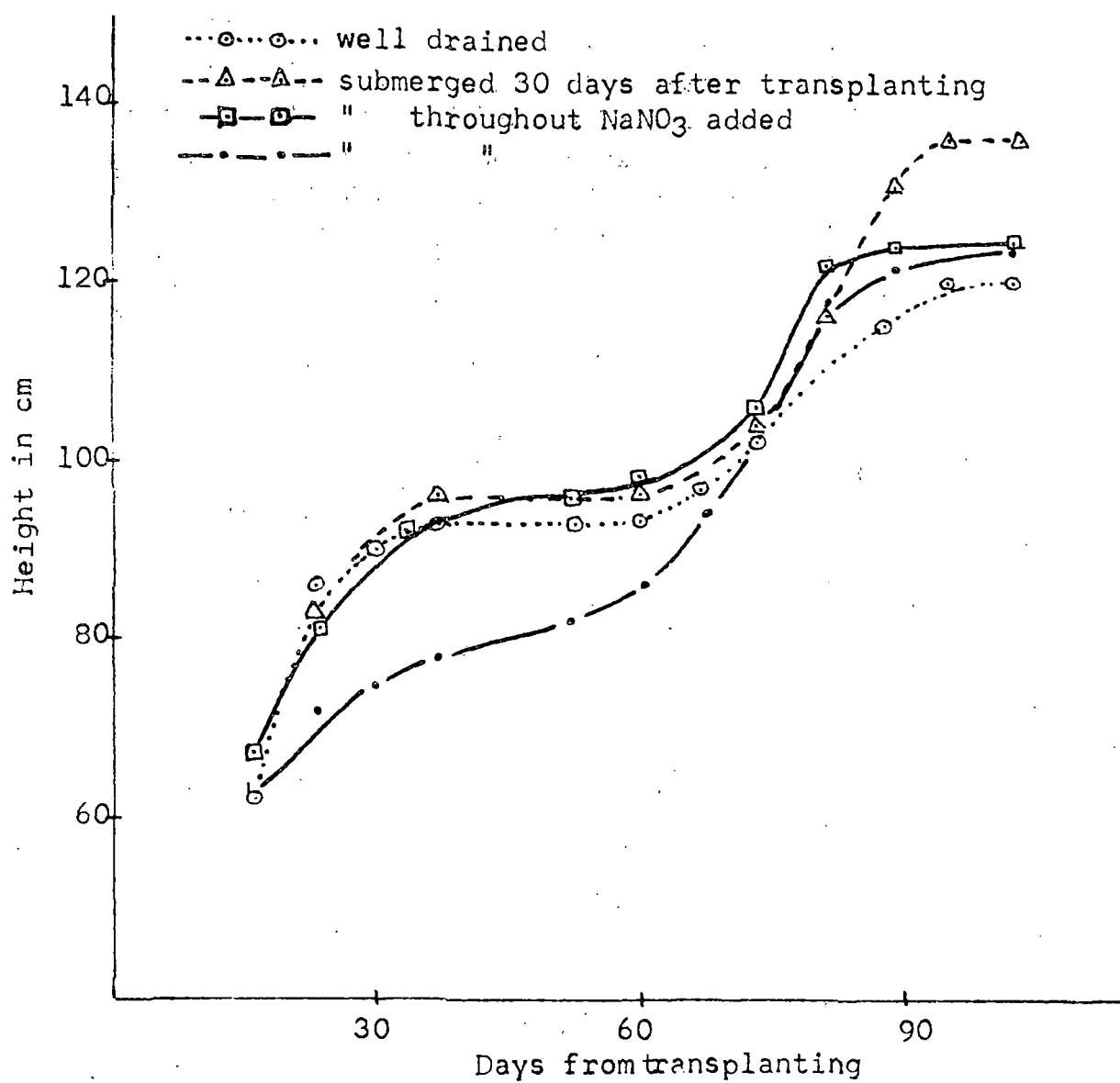
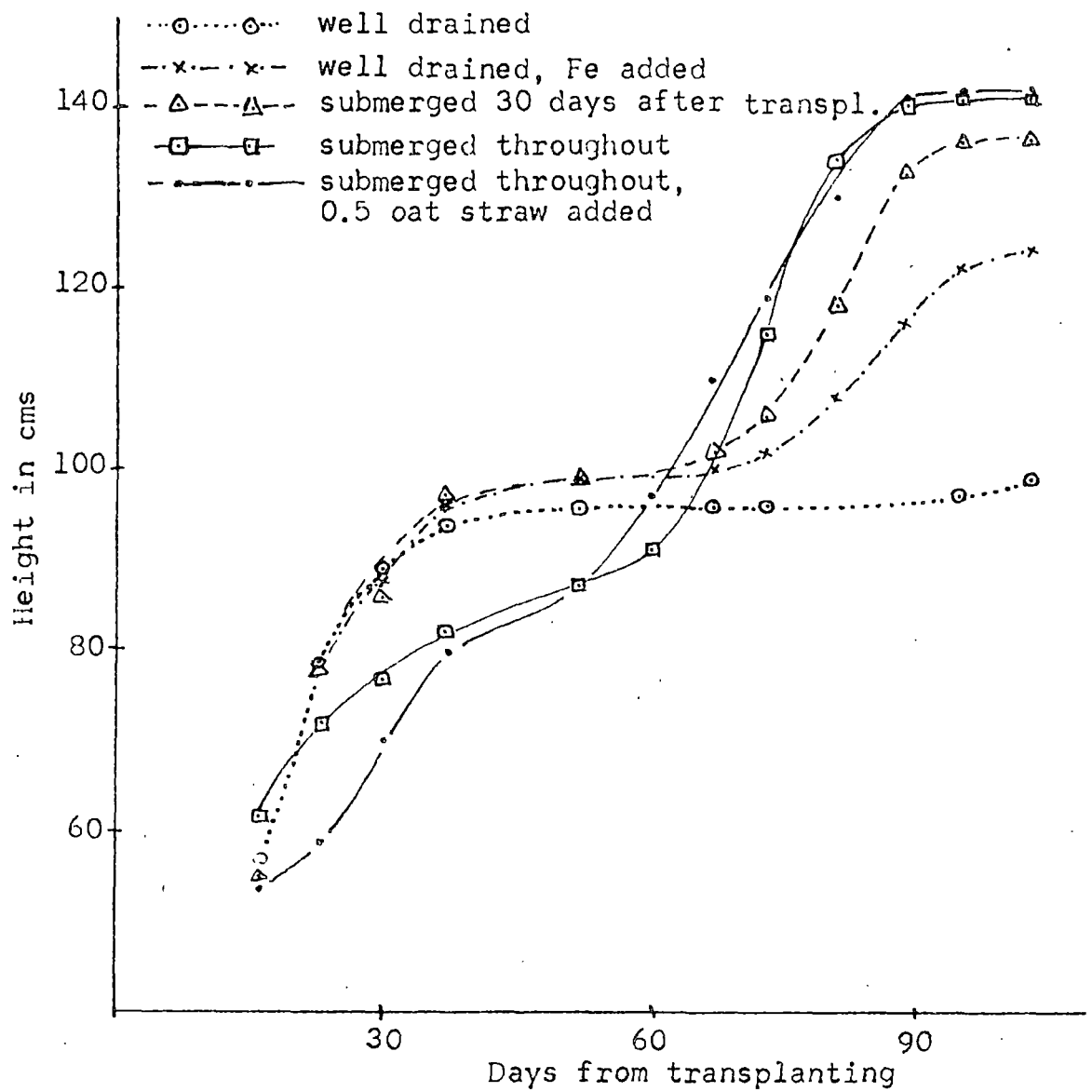


Fig. 39. Growth of rice plants at pH 4.9.



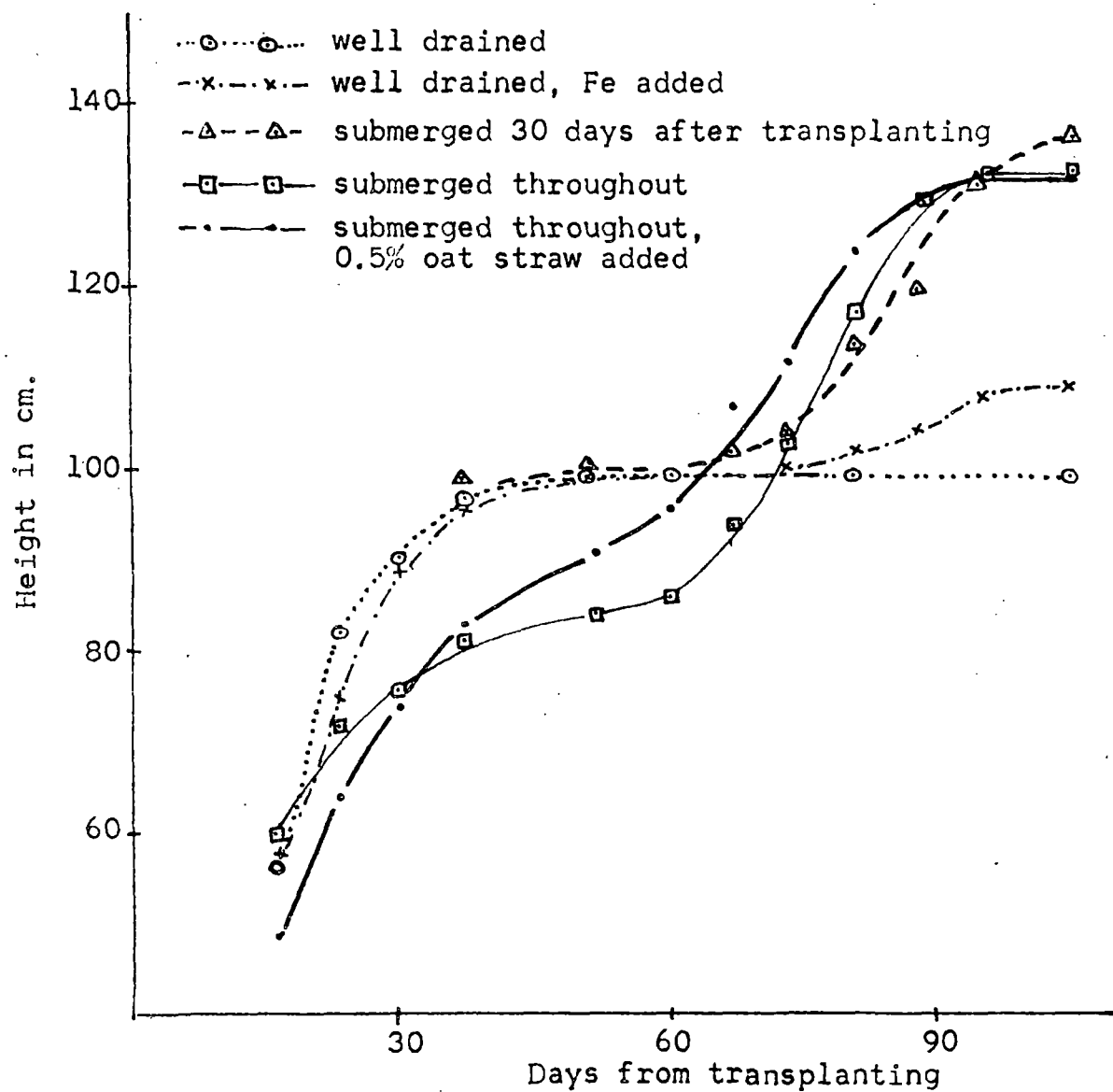
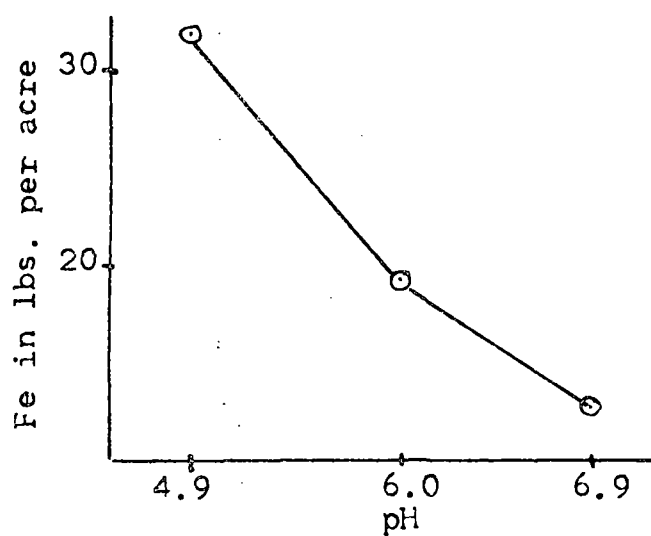
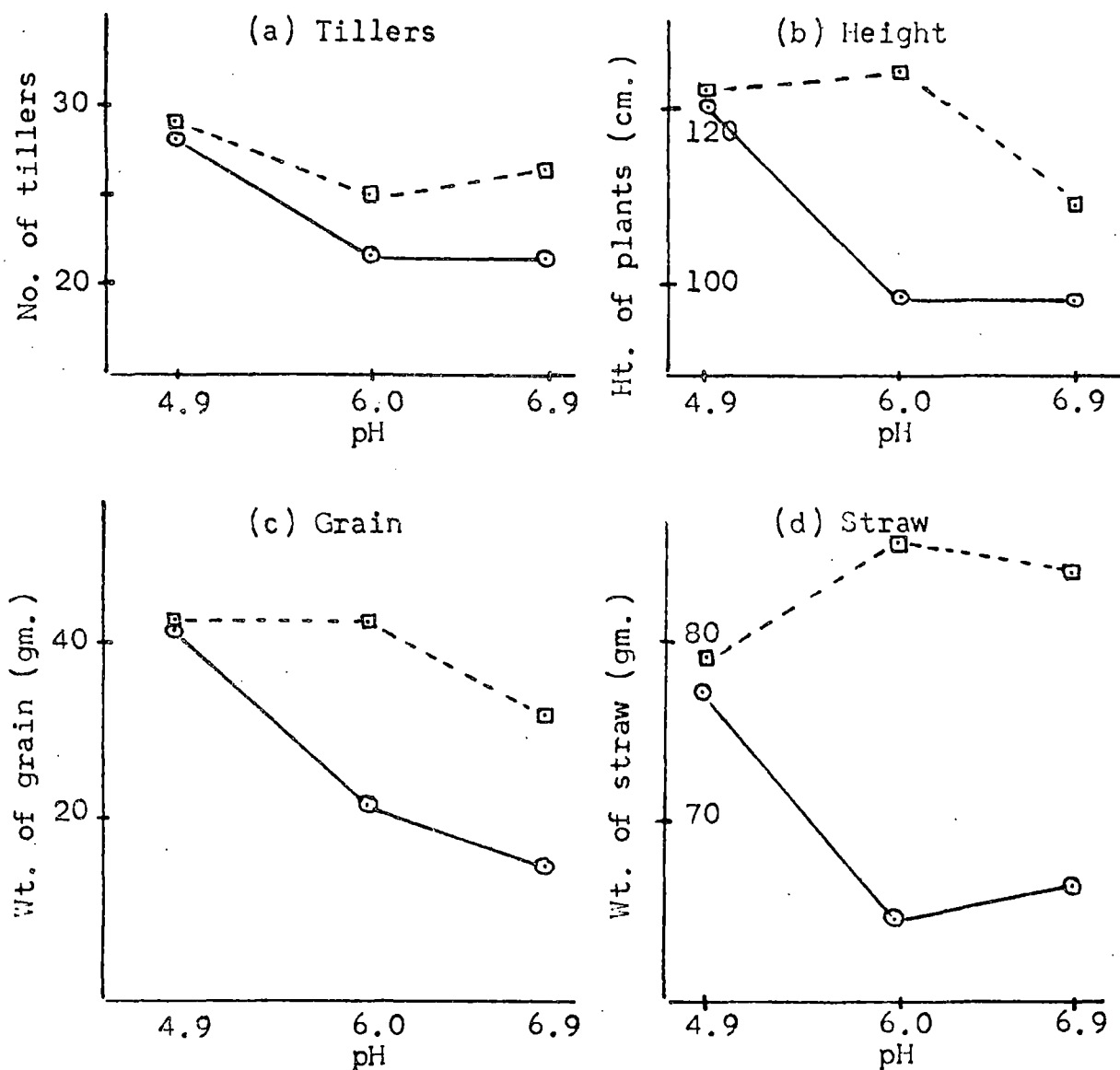


Fig. 41. Growth of rice plants at pH 6.9.

TABLE 22
MEAN GROWTH AND YIELD FIGURES

Treat- ment No.	Treatment	Height cm.	Tillers*	Wt. of Straw gm.	Wt. of Grain gm.
1	pH 4.9, well drained	120.0	29	77.3	41.55
2	pH 4.9, well drained, Fe added	122.3	30	79.3	42.05
3	pH 4.9, submerged on 6/30	136.5	30	96.5	52.00
4	pH 4.9, submerged from start	122.3	31	84.0	27.70
5	pH 4.9, submerged from start NaNO ₃ added	123.0	43	124.5	30.90
6	pH 6.0, well drained	98.7	22.5	64.8	21.85
7	pH 6.0, well drained, Fe added	124.2	26	85.6	42.20
8	pH 6.0, submerged on 6/30	136.4	33	103.9	61.40
9	pH 6.0, submerged from start	141.0	32	105.9	59.60
10	pH 6.0, submerged from start 0.5% oat straw added	141.0	29	100.5	67.35
11	pH 7.0, well drained	98.8	22.5	66.5	17.50
12	pH 7.0, well drained, Fe added	109.3	27.5	84.1	31.60
13	pH 7.0, submerged on 6/30	134.2	33	108.5	57.65
14	pH 7.0, submerged from start	128.2	35	98.6	55.85
15	pH 7.0, submerged from start 0.5% oat straw added	128.0	31	98.7	60.70

* No. of bearing tillers per pot of 6 plants.



—○—○— no Fe added
 ---□---□--- Fe added

Fig. 42. Effect of pH of the well drained soils on the growth and yield of rice.

Fig. 43. Effect of pH on Fe soluble in Morgan's solution.

Among the continuously submerged treatments at pH 6.0 and 6.9, with and without 0.5 percent oat straw there are no significant differences in yield of grain or straw although the number of tillers is slightly lower in the oat-straw treatments. The rapid recovery the oat-straw treatments made during the second half of the period of growth enabled them to equal and even outyield slightly the no-oat-straw treatments, despite the marked retardation they experienced during the first four weeks of growth. Accompanying the dramatic recovery of these treatments was a steady decline in the concentration of soluble iron from a level of approximately 200 p.p.m. 30 days after submergence to about 60 p.p.m. 75 days after submergence. These treatments were also characterized by a relatively high level of NH_4^+ and K^+ throughout the growing season.

The conclusions from this study may be summarized as follows: (i) deficiency of available iron was an important factor limiting the growth and yield of rice on the well drained soils; (ii) delaying submergence of the acid soil for 30 days was extremely beneficial to rice; (iii) nitrate retarded the reduction process and had a decidedly beneficial effect on rice grown on the acid, submerged soil; (iv) the injurious effects of excessive amounts of oat straw were short-lived in the pH 6.0 and 6.9, submerged soils.

6. General Summary and Conclusions

Although rice is almost universally grown on submerged land no physiological reasons have been given for the benefits of this practice. The chemical regime in a submerged soil is so different from that in a well drained soil that it seemed very likely that the benefits of submergence might be associated partly with peculiar chemical conditions that are obtained in a submerged soil.

Chemically, the root zone of a submerged soil is characterized by a low oxygen tension, a high carbon dioxide concentration, the presence of large amounts of reduced iron and manganese, the virtual absence of nitrate and sulfate, the accumulation of ammonia, and the presence of the products of the anaerobic decomposition of organic matter. There is evidence also that the solubility of silica and phosphate increases on submergence.

The physicochemical changes that accompany submergence are an increase in pH and in specific conductance and a decrease in redox potential.

The deficiency of oxygen per se has no physiological effect on rice for rice roots derive their oxygen supply from the shoot system and do not depend on their environment for oxygen. High concentrations of carbon dioxide, however, are toxic to rice. Fortunately, the carbon dioxide concentration in a submerged soil does not attain injurious levels except perhaps in the initial stages of the anaerobic decomposition of organic matter. The increase in solubility of silica and phosphate are probably beneficial to rice; so is the accumulation of ammonia in moderate amounts. Probably the outstanding beneficial effect of submergence is the increase in the availability of iron for there is abundant evidence that the iron requirement of rice is much higher than that of most crop plants. There is evidence also that an excess of reduced substances, especially iron and manganese, may be toxic to rice. These two elements, therefore, merit more than passing comment.

The reduction of iron and manganese in a submerged soil is almost entirely a consequence of the anaerobic metabolism of soil bacteria and proceeds most rapidly under conditions that favor the accumulation of the partially oxidized metabolites. These conditions are the presence of decomposable organic matter and the absence of nitrate. The presence of nitrate, probably by virtue of the high oxidation-reduction potential of the $\text{NO}_3^- - \text{NO}_2^-$ system, retards somewhat the reduction of manganese, but retards considerably the reduction of iron.

The bulk of the iron and to a lesser extent of manganese are probably present in the solid phase as exchangeable ions, as hydroxides, carbonates, sulfides, and perhaps also as insoluble organic complexes. The distribution of reduced iron and manganese between the solid and the liquid phases is governed by ionic equilibria involving Fe^{+2} , Mn^{+2} ,

CO₂, H₂S and pH. Those for iron may be represented by the following equations:

$$p \text{ Fe}^{+2} = 2\text{pH} - 10.8$$

$$p \text{ Fe}(\text{HCO}_3)_2 = 2.38 + 1/3\text{pH}_2\text{CO}_3$$

$$p \text{ Fe}^{+2} = 2\text{pH} - 3.5 - \text{pH}_2\text{S}$$

where p denotes the negative logarithm of the concentration of the component in mols per liter.

The marked influence of pH on the concentration of ferrous iron in solution in an anaerobic soil is apparent from the first equation. The actual concentration of iron may be considerably in excess of that permitted by ionic equilibria, owing to the formation of soluble organic complexes by iron and the products of anaerobic decomposition of organic matter.

Manganese is much more readily reduced and more soluble than iron and it is only the low manganese content of soils that prevents a submerged soil from being deluged with soluble manganese.

The available information strongly suggested that the better growth of rice under submerged soil conditions may be associated with the increase in availability of iron while certain physiological diseases of rice described in the literature appeared to be related to an excess of reduced substances. It was therefore surmised that if rice were grown over a sufficiently wide range of reducing conditions it might be possible to delimit the range in which rice would not be affected by a deficiency of iron on the one hand and an excess of reduced substances on the other. It was believed this range could be characterized physicochemically by pH, specific conductance and redox potential and chemically by the concentrations of iron, manganese, nitrate, nitrite, ammonia and oxidizable matter in the soil solution and also the concentration of iron and manganese in Morgan extracts of the soils. The range of reducing conditions was attempted by varying the pH, organic matter content and drainage level of the soil. The influence of these three factors on rice was studied in a 3x3x3 factorial experiment in a greenhouse. The three pH levels were 4.9, 5.7, and 6.0; the organic matter levels were 0.0 percent, 0.2 percent and 0.4 percent added oat straw; the drainage levels were well drained, submerged with vertical drainage at the rate of 0.4" per day, and submerged with no drainage.

The well drained soils were characterized by a high redox potential, a low specific conductance, a lower pH, an extremely low concentration of iron and manganese in the soil solutions, and much poorer growth and yield than the submerged treatments. Among the well drained soils yield decreased with increase in pH and this was paralleled by a decrease in iron extractable in Morgan's reagent.

The submerged soils with drainage, regardless of initial pH and oat-straw levels, tended to be very similar in their chemical composition

and physicochemical properties. These soils all showed a rapid decline in redox potential and specific conductance but an increase in pH during the first two weeks of submergence. There was a simultaneous increase in iron and manganese and the disappearance of nitrate. Thereafter, the concentration of iron in the percolates got stabilized around a level of about 100 p.p.m. while manganese showed a slight gradual decrease with time. The loss of iron from these soils during the season of 110 days corresponded to about 600 lbs. Fe per acre; that of manganese was about 70 lbs. Mn per acre. The remarkable feature of these submerged treatments was the uniformity of yields, like the chemical analyses, over widely different pH and oat-straw levels. Drainage did not have the expected effect of giving a range of intermediate redox potentials but it did provide a range of intermediate concentration of reduced products.

The submerged no-drainage treatments showed the pH and oat-straw effects in a very pronounced form. The pH 4.9 treatments were characterized by incredibly high concentrations of iron and high concentrations of manganese in the percolates during the greater part of the growing season. These were further enhanced by oat straw. But at no stage did the concentration of water soluble iron exceed 5 percent of the total iron in the reduced state. These treatments exhibited to a marked degree the brown spots, reddish discoloration, leaf scorch and restricted root growth -- symptoms associated with "mentek" disease of rice in Java, "penyakit merah" in Malaya, and browning disease in Ceylon.

The high oat-straw submerged no-drainage treatments at the higher pH levels also showed high iron and manganese concentrations but the injurious effects were apparently shortlived for the plants made rapid recovery about heading time. Yields were generally of the same order as those of the submerged with-drainage treatments.

The best yields of straw and grain were associated with the no-oat-straw submerged treatments at pH 5.7 and 6.0. These soils were characterized by a high redox potential, a high nitrate concentration and low iron and manganese concentrations for about four weeks following submergence. Apparently these soils represented a zone of reduction in which the rice plants did not suffer from a deficiency of iron nor an excess of reduced products.

In a subsequent experiment several of the observations described above were confirmed and certain other points further elucidated.

The decrease in yield of rice grown under well drained conditions with increase in pH and its association with reduced availability of iron was confirmed. It was noted further that unfavorable influence of high pH was largely eliminated by the daily addition of small amounts of ferric sodium ethylene-diamine tetracetate to these soils. The symptoms associated with high concentrations of reduced substances were noted again in the pH 4.9, submerged-no-drainage treatment. The built-up high concentrations of reduced substances was considerably reduced by the addition of sodium nitrate and almost eliminated by delaying submergence for

thirty days after transplanting. The toxic effect of an initial high concentration of reduced products was found to be short lived at pH 6.0 and 6.9 under the favorable climatic conditions of this experiment.

The results of these investigations suggest that: (i) a combination of low pH, high organic matter and complete absence of drainage may cause a physiological disturbance similar to the "mentek" disease of rice; (ii) this disturbance may be corrected by subsoil drainage, delaying of submergence, and the application of sodium nitrate; (iii) a combination of pH near neutrality, presence of nitrate and absence of organic matter and of drainage is conducive to high yields; (iv) a low pH is favorable to the growth of rice under upland conditions.

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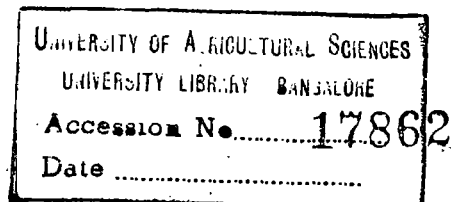
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