CHANGES IN REDOX POTENTIAL AND PHOSPHORUS AVAILABILITY IN SUBMERGED SOILS

by

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INTRODUCTION

Submerged fields are one of the requirements for successful rice cultivation. Rice fields have to be maintained under submerged condition for a period of at least three to four months. Submerged soils differ considerably in electrochemical and biological properties from upland soils. Such submerged soils are characterized by a scarcity of oxygen due to its initial displacement from the soil profile by water and rapid consumption by various soil microorganisms. Such a condition is often described as "anaerobic." Development of anaerobic conditions in soil, temporarily or permanently, plays a marked role in determining the availability and uptake of essential elements by plants. As it has a direct bearing on crop yields and plant welfare, the availability and subsequent changes in plant nutrients is of much economic importance and considerable scientific interest.

Of the elements presently regarded as essential for plant growth, the fate of phosphorus, either native or applied in soil, is intricate and as a result workers are interested in it in different parts of the world. On application of a readily available form of phosphorus ($H_2PO_4^-$ or $HPO_4^=$) to soil, it is converted into less soluble forms through various agencies following complex reactions. As a result the applied or even native phosphorus becomes restricted in its mobility in soil and is rendered unavailable to plants. In submerged soils, the behavior of phosphorus is peculiar and interesting. The anaerobic condition prevailing in submerged soil has a trigger effect, i.e., it leads to peculiar oxidation-reduction conditions and changes in such conditions do exert some influence on forms of soil phosphorus.

Most of the inorganic fraction of soil, being predominately in an oxidized state, is therefore subjected to reduction under submerged conditions. Iron and manganese are elements that may be reduced. Organic matter is mostly in the reduced state and is therefore subjected to oxidation when proper conditions prevail. The oxidation-reduction processes are mainly due to activity of soil microbes, which derive their energy from these processes (Rabinovich, 42). As a side effect considerable Fe(ic) is reduced to Fe(ous) which is more soluble. Consequently the iron-phosphates, which are considered insoluble, stable and hence unavailable forms of phosphorus in soils, are brought into solution to some extent. This phenomenon has significance in submerged soils, especially to the rice crop. There are evidence which show that the phosphate combining with iron in soil is relatively more soluble in submerged soil because of such reduction of iron from ferric to ferrous state. The soils under submerged conditions may therefore be more fertile from the point of view of phosphate availability. Therefore investigations of phosphate changes in submerged soils, which may prove valuable to rice culture, are considered significant. By knowing the changes, one may direct attempts to hasten or increase phosphorus availability under submerged conditions so as to meet the demand for phosphorus by the rice crop during its vegetative growth. In this connection a lot of work has been reported in Japan, India, China and some in the United States.

The oxidation-reduction condition of soil, which can be measured with reasonable accuracy by use of suitable electrodes, may serve as an index in estimating the availability of iron-phosphate in soils and especially under submerged conditions. The changes in redox potential and available phosphorus in soils and their interrelationships, are studied and discussed.

THEORETICAL CONSIDERATIONS

Redox Potential

Oxidation is the process in which ions, atoms or substances emit negative electrons with the liberation of a definite quantity of energy. Reduction is the process in which ions, atoms or substances accept negative electrons. In a system oxidation is always accompanied by reduction and vice versa.

$$\boxed{\begin{array}{c}\text{Reduced}\\ \text{state}\end{array}} \quad \underset{\text{reduction}}{\overset{\text{oxidation}}{\rightleftharpoons}} \quad \boxed{\begin{array}{c}\text{oxidized}\\ \text{state}\end{array}} \quad + e^-$$

Oxidation or reduction state of any chemical system is expressed in terms of either an oxidation potential or reduction potential and abbreviated as E_{ox} or E_h respectively and is measured in volts or millivolts. In most soils literature reduction potential (i.e., redox potential) is often used. Hence redox potential will be used throughout this report.

Redox potential of a chemical system may be defined as a measure of the tendency for a reduction reaction to occur. The reduction process involves acceptance of electrons, i.e., a change in valence state. Hence the presence of an element or ion having variable valence is a necessary prerequisite for an oxidation-reduction reaction. The mineral part of soil contains iron, manganese, phosphorus and others which can undergo valence change and thus may exist in an oxidized state in well aerated soils and in a reduced state in anaerobic soils. According to Merkle (36) the valence possibilities of common constituents in the mineral and organic fractions of soils are: Fe, 2, 3, 6; Mn, 2, 3, 4, 6, 7; C, 2, 3, 4; N, 3, 5; S, 2, 4, 6; and P, 3, 5.

A greater positive value of redox potential of soil indicates more tendency for reduction to occur in soil, or in other words, soil is in a well oxidized state. Conversely for a greater negative redox potential value of soils, there is less tendency for the soil to undergo further reduction, i.e., the soil is in a highly reduced state. Jackson (24) has suggested an arbitrary scale of redox potentials of soils (Table 1) for classification according to its oxidation condition.

Table 1. Scale of reduction potentials measured with a platinum electrode. For the soil conditions given, the measurement is in situ.

Oxidation condition of soil	Redox Potential	
	volts	millivolts
Very well oxidized soil	0.800	800
Well oxidized soil	0.500	500
Moderately well oxidized soil	0.300	300
Poorly oxidized soil	0.100	100
Much reduced soil	-0.200	-200
Extremely reduced soil	-0.500	-500

Lamm (30) suggested the term "redox level" in place of the term "redox potential" as an expression for the mean reducing or oxidizing activities in dry soil samples. Recently Jeffery (25), while defining the state of reduction of a paddy soil, has used the empirical terms (1) oxidizing conditions, (2) healthy reducing conditions and (3) extreme reducing conditions.

Factors affecting redox potential in soils: The redox potential of a soil-water system as it exists in nature, is an extremely variable physico-chemical property and is influenced by numerous factors. They are as follows:

1. Nature and amount of poising agents. Substances capable of absorbing electrons are oxidizing agents. Reverse is true for reducing agents. All elements in the mineral and organic fraction of soil do not have the same fugacity. Secondly if an element has two or more valences, each valence has its own characteristic oxidation potential as governed by the binding energy of the electron in the atom and energy of solvation of the atom. The experimental evidences, however, have shown that iron is easily oxidized, manganese is easily reduced. Similarly sulphur and nitrogen undergo reduction rather easily. Thus the nature and amounts of such oxidizing or reducing agents are found to dictate the large variation in redox potential of soils.

2. Presence of fresh organic matter. Carbon, being capable of changing its valence state under favorable conditions, comprises 56 percent of the organic matter fraction of soil, and plays one of the major roles in determining redox potential of soil. In most reduction processes in soil microbial activity is largely involved. Readily oxidizable organic matter serves as food material--energy source--for soil microbes. Thus the presence of organic matter speeds up reduction of minerals in soil. Therefore the more oxidizable organic matter, the more rapid the changes in reduction potential will be within the first few days after submergence.

3. Soil aeration. Complete absence or scarcity of oxygen in soil air necessitates the micro-organisms to derive their energy requirement from other oxidized metals, ions or substances. It is supposed that under submerged conditions (anaerobic) most energy required by microbes is derived by reduction of elements like Fe^{+3} to Fe^{+2} or Mn^{+7} to Mn^{+2}. In well aerated soils aerobic micro-organisms do not have such a problem, consequently the soil redox potential values are high and positive. In poorly aerated soils they are low

and in extreme cases negative. Soils saturated with natural gas develop low redox potentials and degree of natural gas saturation determines redox potential of such soil.

4. Soil moisture. Soil air and soil moisture, present in voids, affect the redox potential of soil simultaneously. Water is retained in soil after partial or complete displacement of soil air depending upon moisture content and time. With an increase in successive amounts of water in soil, soil aeration decreases with an accompanying reduction in the redox potential of soil. In brief the effect of soil moisture and aeration on redox potential of soil cannot be separated, i.e., it is interdependent.

5. Soil pH. The soil pH seems to be very closely associated with the redox potential of soil. The hydrogen ion concentration of soil-water system affects the degree of ionization and hence alters the redox potential of soils. However the pH effect on redox potential of soil is inconsistent. It is hypothesized that in many soil-water systems, the E_h values increase by about 59 mv per each unit lowering of the pH value (Fig. 1).

6. Microbial activity. Soil microbes, especially those thriving under anaerobic conditions, are mainly responsible for oxidation of organic matter, and in turn reduction of the mineral fraction of soil. Hence more activity may lower the redox potential values at a rapid rate.

7. Climate. Redox potential variation in soils from season to season is ultimately the sum total effect of the factors described so far. Many soils, in humid areas, have high water tables in the spring but the level lowers as the season advances. Such variation in height of water table is also known to influence the redox potential of soil. Sharapov (47) reported that when the weather was hottest the E_h values of soils rich in organic matter fell to -200 to -250 mv. Stobe (50) found the highest oxidation potentials of soils in summer.

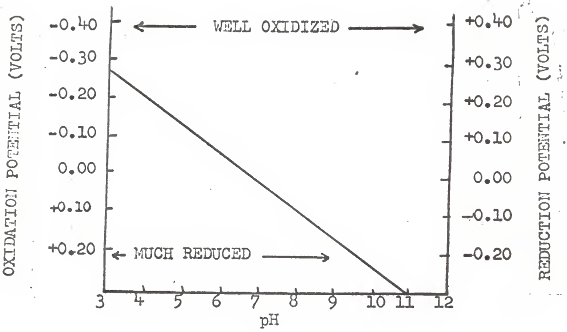

Fig. 1. THE RELATION OF REDOX POTENTIAL OF SOIL TO SOIL pH. INCREASING pH DECREASES THE REDOX POTENTIAL OF SOIL (Jackson, 24)

Measurement of Redox Potential: The redox potential as defined before is an expression of intensity of oxidation and reduction conditions. The measure of redox potential is a measure of electron pressure existing in the soil at equilibrium. In oxidized soil, there will be more tendency to emit electrons than to receive, and vice versa in a reduced soil. The electron pressure can be measured if a platinum electrode is placed in close contact with the soil-water system. The electrode, which has attained potential equilibrium, serves as one half cell. Either a normal or saturated calomel electrode is usually used as the standard reference half cell (Fig. 2). The potential difference measured is the ratio of the total oxidizing intensity of system to the total reducing power of the system.

It is expressed by the following modification of the Nernst equation adapted to concentration cells by Peters:

$$E_h = E_o + \frac{RT}{nF} \ln \frac{[ox]}{[Red]}$$

where

E_h = the redox potential of a system measured

E_o = the standard redox potential of the reference electrode

R = the gas constant

T = temperature ^{o}K (Kelvin)

n = valence change

F = the Faraday of electricity 96500 electrons/equivalent

ln = natural logarithm to the base e

$[ox]$ = the activity of the oxident

$[Red]$ = the activity of the reductant.

On evaluating constants namely R, T, n, F and converting natural logarithm to the common logarithm, the equation becomes:

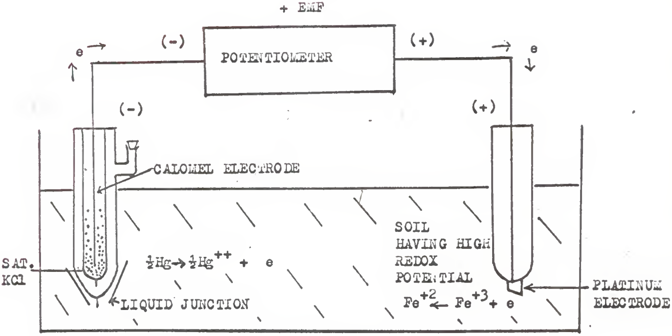

Fig.2. THE ELECTROCHEMICAL CELL DIAGRAM SHOWING THE NEGATIVE (ELECTRON EMITTING) ELECTRODE ON THE LEFT, i.e. THE HALF CELL UNDERGOING OXIDATION AT THE LEFT. (Jackson, 24)

$$E_h = E_o + 0.059 \log\frac{[ox]}{[Red]}$$

This potential difference measurement is analogous to pH measurement. The same pH meter, a potentiometric hook-up, can be made use of to measure e.m.f., except that a blackened platinum electrode is used in place of the hydrogen or glass electrode. The function of black, colloidal platinum on the platinum electrode, is to absorb oxygen from the soil air and thus to form an oxygen electrode (OH^- , $\frac{1}{2}\ O_2$). A calomel half cell is usually used as a reference cell but the e.m.f. is finally referred to the normal hydrogen electrode taken as zero.

Calculation of the Redox Potential of Soil: The redox potential of soil is calculated by the equation:

$$\underset{\text{Observed}}{\text{E.M.F.}} = E_{h_2} - E_{h_1}$$

where

E_{h_2} = redox potential of a system undergoing reduction.

E_{h_1} = redox potential of a system undergoing oxidation.

The above equation for a Beckman potentiometer using a saturated KCl calomel half cell becomes:

$$E_h\ (\text{soil}) = \pm \underset{\text{observed}}{\text{E.M.F.}} + 0.2415$$

It is possible to calculate the hypothetical redox potential at some reference pH value other than that existing. It can be calculated directly from the following equation: (Jackson, 24)

$$\underset{\text{at desired pH}}{E_h} = \underset{\text{at measured pH}}{E_h} + 0.059\ (\text{soil pH} - \text{desired pH})$$

Different practical methods of determination of redox potential of soils and their instrumentation have been suggested by workers. Soils workers have used the procedure proposed by Brown (7) with slight modifications. These modifications call for: omission of centrifugation, the extension of time from insertion of electrodes to measurement, and use of an auxilliary electrode to determine an approximate potential. Some investigators have devised instruments for the measurement of soil redox potentials. Yamanaka (53) assembled a vacuum potentiometer, using ordinary radio-tubes. Nishigaki et al. (37) devised a floating internal-shielded E_h meter that can be used to measure the redox potential of a very minute mass. Another portable instrument for E_h measurement in situ, devised by Matsuo and Kato (32) consists of a single pentode 1T4 connecting as a single form, a micro-ammeter working from 0 to 500 µA, two batteries and other parts. It has an advantage because such portable meters eliminate the undesirable effects caused by disturbances of soil and changes in E_h during transport.

Yu and Li (55) have described a method of characterizing poizing systems of the soils based on the principles of depolarization. They used two types of electrodes as the anode and cathode, i.e., quinhydrone electrode in 1 N HCl solution and Pb-electrode immersed in lead acetate solution. The elaborate practical procedure of soil E_h measurement in laboratory and in situ is given by Jackson (24).

In the interpretation of E_h values of soil, utmost care should be taken, because the E_h values are not concordant as soils are poorly poised. The redox potential registers the balance or level of electron pressure, i.e., it determines the degree of oxidation-reduction intensity in soil-water system under a given set of conditions. It does not measure the capacity value.

Phosphorus Behavior in Soils

The forms of phosphorus compounds in upland soils do not differ much from the forms of phosphorus in submerged soils, however, there seems to be a significant difference in the forms which are dominant.

In brief soil phosphorus forms can be summarized as follows:

A. Phosphate ions in soil solution

B. Organic phosphorus compounds
   1. Phytin and its derivatives
   2. Nucleic acid and its compounds
   3. Phospho-lipids

C. Inorganic phosphorus compounds
   1. Calcium phosphates, e.g., different types of apatites, mono, di, and tri calcium phosphates
   2. Iron and aluminium phosphates
   3. Other phosphates of Mg, Mn, etc.

D. Phosphate ions adsorbed by colloids.

These various forms of soil phosphorus are somewhat dynamic and exist more or less in equilibrium condition. When fertilizer containing soluble forms of inorganic phosphorus are added to soil, it is known beyond doubt that fixation of added phosphorus takes place in soil. Such fixation of phosphorus in soils may be defined as the process whereby readily soluble phosphorus is changed to less soluble forms by reaction with organic or inorganic constituents of soil and its availability to plants is decreased. The type of reactions of fixation of soluble phosphorus are mainly placed in three general categories:

(a) Adsorption reactions

(b) Reactions involving isomorphous replacement

(c) Double decomposition involving solubility product reactions.

$H_2PO_4^-$, $HPO_4^=$ and $PO_4^{\equiv}$ ion species are involved in these reactions. All these reactions occur in submerged soils with varying degree of intensity as the electrochemical and biological properties of submerged soils and uplands differ. So to date a lot of work has been reported in order to investigate the various factors influencing the complex phenomenon of phosphorus fixation, but much remains to be understood. The various factors suggested so far may be segregated into two main groups: (1) factors influencing the amount of available phosphorus in soil, may be termed as "quantity factors", and (2) factors influencing the nature or quality of form of soil phosphorus with regards to availability and may be called "quality factors".

Quantity factors are as follows:

1. presence of sesqui oxides
2. presence of organic matter
3. nature and amount of clay
4. soil moisture
5. soil aeration
6. soil pH

Quality factors are as follows:

1. time or aging
2. degree of crystallinity of product of fixation process
3. chemical nature of soil phosphorus fractions like aluminium phosphate, iron phosphate and calcium phosphate.

If these quantity and quality factors are known it seems to be possible to speculate--though not accurately--as to the amount of added or native soil phosphorus that may be available under a given set of conditions. But in practice it is impossible with our present knowledge. However with available information, qualitative determination of soil phosphorus availability can be made using the following expression:

$$\triangle P = f\left(\frac{pH,\ O.M.,\ clay,\ H_2O,\ O_2}{R_2O_3,\ T,\ C,\ K_s}\right) t$$

where

$\triangle P$ = quality of soil available phosphorus

pH = H ion concentration in soil

O.M. = organic matter content

clay = amount and nature of clay content

H_2O = percentage soil moisture

O_2 = degree of aeration

R_2O_3 = sesqui oxide content

T = soil temperature

c = chemical nature of form of soil phosphorus

K_s = degree of crystallinity of P fixation product

t = time factor.

Fate of Applied Phosphorus

Soil phosphorus availability appears to be primarily a function of time when other factors are constant. When soluble inorganic phosphorus is added to soil two kinds of phosphorus compounds are formed immediately: (1) fresh precipitates of calcium, iron, or aluminium phosphates, and (2) similar compounds formed on the surface of either $CaCO_3$ or Fe and Al oxide particles. These freshly formed phosphorus compounds are still fairly readily soluble and available to plants, since most of the reaction is limited to surface of the particles. The total surface area is high and consequently the availability of phosphorus is reasonably rapid. Further changes result in reduction of surface area of these phosphate compounds and corresponding decreased availability. According to Chang and Jackson (9, 10) precipitated calcium and aluminium phosphates gradually change to insoluble iron and calcium phosphates with time. This change in solubility with time is considered as an aging effect. Iron activity in soil is associated with a decrease in soil pH (Kittrick and Jackson, 29). Ultimately iron and aluminium phosphates are slowly converted into occluded (coated with an iron oxide) form. Generally this is the final product of applied soluble phosphorus in course of chemical weatherings in acid soils since it is considered to be the most stable compound. These chemical transformations of soil phosphorus fractions are well noticed in acid soils, to some extent in neutral soils and at times in alkaline soils to lesser intensities. In case of calcareous soils, calcium phosphate forms like carbonate, hydroxy or oxy apatites are found most dominating.

In submerged soils the changes are more or less the same, but due to reducing conditions there is a possibility of ferrous-phosphate formation in place of ferric phosphate compounds. The ferrous phosphate compounds are relatively more soluble and hence may be considered as more available to plants.

The presence of organic matter in soil has its role in determining the fate of applied and native phosphorus in uplands as well as in submerged soils. Applied soluble phosphorus in soil is likely to be utilized by soil micro-organisms for building their own body tissue. Such utilization of available phosphorus is commonly known as temporary fixation of phosphorus in soil. With time soil microbial tissue and the organic fraction undergo decay and thus temporarily fixed phosphorus is again released into the soil and converted into available inorganic forms. This process is also called "mineralization of phosphorus in soil." It has much practical significance from a phosphorus availability point of view. The chelating action of soil organic matter also increases the phosphorus availability in soil by the formation of complex organo-metallic compounds of iron and aluminium.

LITERATURE REVIEW

Changes in Redox Potential

In submerged soils the iron content, which determines the final fate of soil phosphorus in acidic soils, is largely responsible for the development of reducing conditions, i.e., ferrous-ferric system greatly influences electro-potential differences in soil. Available literature indicates that there is a definite effect of submergence on iron content of soil. Osugi (38), Reed and Sturgis (43) noticed that soil solution from water-logged soils contained higher concentration of iron than aerated soil solution. Pearsall (40) observed that in a marsh the exchangeable ferrous iron was as high as 248 mg/100 gm of dry soil. Poonamperuma (41) obtained 147 and 80 ppm of Fe(ous) in the soil percolate after 67 days of submergence of a soil of pH 6.0, treated with and without 0.4 percent oat straw respectively. De and Mandal (16) found a gradual increase in Fe^{+2} content of the percolate from two soils kept under a water-logged condition for 90 days. Hence it can be concluded that a submergence reduction of ferric iron to ferrous iron may be the main reason for increased solubility of iron. The transformations of ferric to ferrous iron may be due either to a chemical or biological reaction. The differences in redox potentials resulting from changes in the oxidation condition of inorganic constituents of soil, primarily iron, have been noticed by many workers. Osugi (38), Sturgis (51), Aomine (2), Mckenzie et al. (33), Mandal (31) and many others have investigated the effects of submergence on redox potentials of soils and obtained similar results:

(a) the redox potential of a surface layer approaches a minimum redox potential value within a few weeks after submergence; and (b) a fresh supply of organic matter results in a rapid drop in redox potential. The soil structure and rate of drainage were also found to affect redox potential of soil. Buehrer et al. (8) noticed a marked decrease in redox potentials as a result of puddling particularly when the soil had been treated with alfalfa. Gillispie (22) reported that the addition of 0.1 percent glucose to water-logged soils caused very pronounced reducing conditions. Shiori and Aomine (49) observed a greatly accelerated decline in redox potentials when a soil was air dried prior to water-logging. Patrick(39) recorded a drop in redox potential from 500 to -100 mv. and increased soil pH from 4.6 to 7.0. Rodrigo and Pollard (44) reported that when normally dry soils were submerged in water the pH increased and E_h decreased in both soils and supernatant liquid, reaching equilibrium values in 80 days. According to Kawaguchi (personal communication) a reducing condition of submerged soil is greatly influenced by a slight change in moisture content of soil prior to water-logging. Smaller the moisture content of a soil before submerging, greater the development of reducing condition in soil after submerging. This is probably due to dehydration and subsequent increase in decomposability of soil organic matter.

In rice soils, the A horizon shows a rapid decline in potentials in comparison with subsoils and uplands. Mckenzie (34) noticed that variations in redox potential with space were correlated with soil horizon. Stobe (50) found that oxidation-reduction potentials decreased with depth. Aomine (2) observed that due to water-logging in well drained soil an oxidized layer was sandwiched in between two reduced layers, but in poorly drained soil the whole soil profile was reduced. Shiori and Aomine (48) drew attention to the fact that oxidized portions are present around living roots in submerged soils, and reported a little higher E_h in soils in the presence of rice plants than in the soils alone. This indicates that rice plants are capable of oxidizing soils. Thus submerged soils are, in general, heterogeneous in redox potentials vertically as well as horizontally--that is, in most submerged rice soils oxidized and reduced portions coexist.

Changes in Soil Phosphorus

The formation of Ca-bonded, Al-bonded and Fe-bonded phosphorus is considered by many to represent a path of phosphate fixation in soils. Metzger (35) found that iron and aluminium oxides (R_2O_3) contents of soil show a high degree of correlation with phosphorus fixing capacity of soil. Ghani and Islam (20) reported that more than 90 percent of the fixed phosphorus was recovered as iron and aluminium phosphates. They showed that chemical precipitation of soluble phosphorus as Fe-bonded and Al-bonded phosphates accounted very largely for fixation in acid soils. Ellis and Truog (18) concluded that montmorillonite will not fix phosphorus when iron and aluminium oxides were removed and the clay saturated with hydrogen. Chang and Jackson (9, 10) reported that the final product of soluble phosphorus added to soil is a complex iron-bonded phosphorus, which is more stable in acid soils. Chang and Chu (11) noticed an increase in the amount of iron phosphate and decrease in Aluminium phosphate and calcium phosphate in rice soils with passage of time. In Taiwan rice soils they noticed that iron phosphate commonly dominates the inorganic soil phosphorus fraction.

Hence it may be postulated that the availability of phosphorus in paddy soils is a function of the magnitude and reactivity of the prevailing Fe-P systems.

Significant changes in electro-chemical and biological properties of submerged soil result in changes in soil-phosphorus availability. Some workers report inconsistent or no response to phosphorus fertilization under submerged conditions even where upland crops responded considerably to added phosphorus. Aoki (1) noticed increased solubility of soil phosphates when rice fields were flooded. Kawaguchi (27) concluded that the solubility of soil phosphorus will increase with the development of reducing conditions in a submerged soil in the case that iron-phosphate is the main constituent of the soil phosphorus. Egawa et al. (17) used P^{32} to trace the behavior of phosphorus added to water-logged soils and noticed similar increased solubility of soil phosphorus. Chin (12) found that the amount of water soluble phosphorus increases with the development of reducing conditions and equilibrium is likely to be attained in 20 to 30 days after submergence. Shapiro (45, 46) reported increased rice yield and total phosphorus uptake under flooded conditions. He concluded that the increase in available phosphorus could be due to either reducing conditions or hydrolysis or both. Davide (15) noticed that a beneficial effect of flooding on phosphorus availability depended on the extent of reduction processes and the Fe content of soil. Basak and Bhattacharya (4) found that the iron and aluminium phosphates in puddled soil decreased from 847 lbs. to 424 lbs./A with the progress of rice crop growth from planting to maturity. Further they concluded that water-logged soils tend to show a unique capacity of regenerating an increasing quantity of available phosphorus during the active period of crop growth. Ghose et al. (21) and Chirkova (13) hold the same view. They found that the reduced conditions prevailing in the water-logged soil increased the soil phosphate availability.

The overall increase in soil phosphorus availability of either native or applied phosphorus under submerged conditions can be attributed to: (1) the increased solubility of iron phosphate due to change from Fe(ic) to Fe(ous) iron and (2) the hydrolysis of soil phosphates brought about by reducing conditions of soil (Fujiwara, 19). Thus the findings suggest that the decrease in redox potential of soil after submergence increases soil phosphorus availability. However limited information is available on the relationship between redox potential and available phosphorus under submerged soils. The objective of the present experiment was to study changes in redox potential and available phosphorus and their relationships under submerged soil conditions.

EXPERIMENTAL METHODS

Surface samples of Cherokee silt loam and Colby silt loam soils were used in the present study (Table 2).

Table 2. General characterization of original soils used in the experiment.

Soil type	Sampling location	pH	Organic matter	Available P lbs./A
Cherokee silt loam	Columbus Experimental Field	6.2	2.0	13
Colby silt loam	Near Garden City	7.6	1.3	21

Five hundred grams of weighed soil were placed in polyethylene (about $1\frac{1}{2}$ pint capacity) rectangular containers. The treatments, in duplicate, were as follows:

1. Moisture. (a) field capacity
   (b) twice field capacity
   (c) submerged.

Field capacity of the soils was determined by pressure membrane apparatus and accordingly calculated amounts of water were added. In submerged condition water level was one inch above soil. These moisture levels were maintained for 75 days.

2. Organic matter. (a) 0 percent
   (b) 1 percent

Dried and powdered alfalfa hay obtained from the Agronomy Farm, Kansas State University, was used as a source of organic matter.

3. Phosphorus. (a) 0 lbs. P/A
   (b) 200 lbs. P/A

Phosphorus was added in form of mono-calcium phosphate (analytical grade).

The soils were sampled at 15 day intervals until the redox potential of the soils reached near equilibrium conditions. Following are the determinations made on each soil sample:

1. Soil pH. It was determined using a Beckman glass electrode pH meter.

2. Redox potentials (E_h). E_h values were recorded in containers without disturbing soil, using a blackened platinum electrode in place of the glass electrode. Saturated KCl calomel half cell was used as standard cell having E_h of 0.2415 volts.

3. Available phosphorus. It was determined by Bray's method (0.03 N NH_4F + 0.025 N HCl) using 1:20 as soil:extractant solution ratio. Simultaneously on each soil sample, moisture determination was made.

EXPERIMENTAL RESULTS

Changes in Redox Potential

Most research has shown that in submerged soils the redox potential (E_h) of soils decreases as a result of strongly developed reducing conditions. The changes in E_h values of soil which were calculated with reference to the original soil pH values, are given in Appendix I. The data show close agreement with previous work reported. As indicated by Figures 3 and 4, E_h values at field capacity remained fairly constant in the Cherokee silt loam soil from the Columbus Experiment Station and increased slightly (approximately 100 mv) in the calcareous Colby silt loam soil from Garden City. The effect of submergence on E_h values of both soils was the same. The soils at twice field capacity had intermediate E_h values suggesting that intermediate reducing conditions developed. As a result of submergence a sharp fall in the E_h values of the Cherokee silt loam soil was noticed within the first 15 days and within 30 days in case of the Colby silt loam soil. Total reduction in E_h values was from 631 to 147 mv and 477 to 88 mv in the Cherokee silt loam soil and the Colby silt loam soil respectively under submerged conditions without organic matter. In Colby silt loam, at twice field capacity after a slight increase in E_h values up to 45 days, the redox potentials started decreasing.

The effect of addition of fresh organic matter (powdered alfalfa hay) on redox potential at twice field capacity and under submerged conditions was more pronounced than at field capacity. At the end of the experiment, the difference between E_h values, with and without organic matter under submerged conditions was 52 mv and 63 mv in the Cherokee silt loam and Colby silt loam

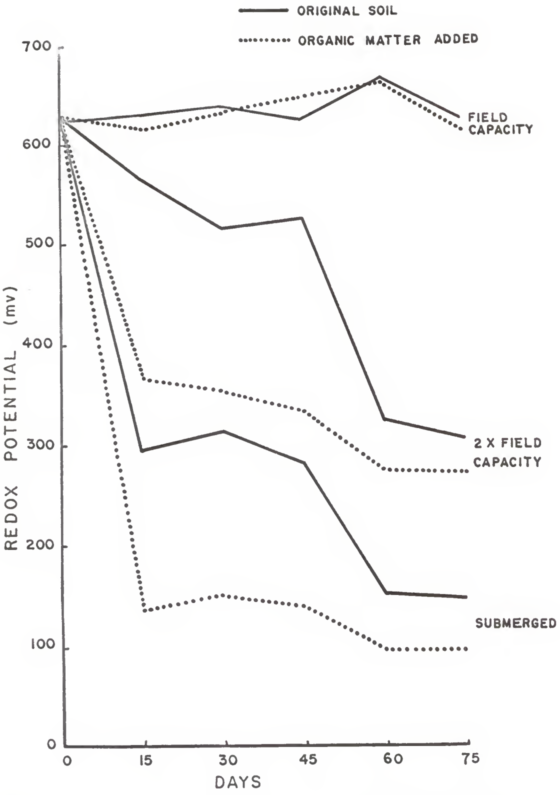

Fig. 3. CHANGES IN REDOX POTENTIAL (E_h) AT DIFFERENT LEVELS OF MOISTURE AND ORGANIC MATTER IN CHEROKEE SILT LOAM SOIL.

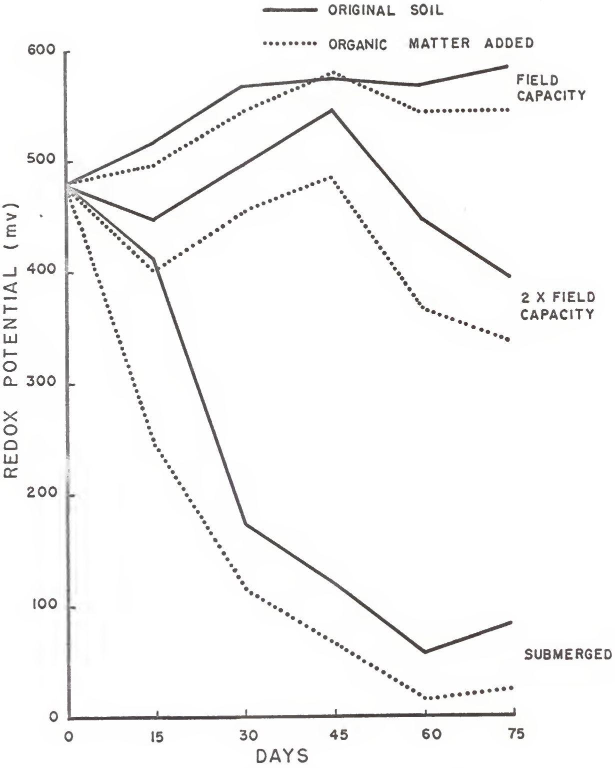

Fig. 4. CHANGES IN REDOX POTENTIAL (E_h) AT DIFFERENT LEVELS OF MOISTURE AND ORGANIC MATTER IN COLBY SILT LOAM SOIL.

respectively. The sharp decrease in E_h values was accelerated by addition of organic matter during the first 15 days in either soil (Fig. 3, 4). The decrease in redox potential after the sharp fall in their values was gradual until the end of the experiment. According to a scale of redox potential measured with a platinum electrode, proposed by Jackson (24), both soils were well oxidized initially but after 75 days under submerged conditions, they were in a poorly oxidized state.

Changes in Bray's Available Phosphorus

Changes in availability of native soil phosphorus and applied phosphorus in the soils as measured by Bray's method, are summarized in Appendix II and Figures 5 and 6. With some exceptions, available phosphorus increased with time. At field capacity, changes in availability of native phosphorus were less variable as compared to changes in availability of applied phosphorus. Soil moisture, with or without organic matter, had a definite influence on availability of both native and applied phosphorus in Cherokee silt loam soil. As indicated in Figure 5 for the Cherokee silt loam the overall availability of native as well as applied phosphorus, as a function of time, could be summarized as follows:

P available at field capacity < at twice field capacity < submerged condition

However, this sequence did not hold for phosphorus in case of the Colby silt loam. The availability of applied phosphorus showed large fluctuations and soil moisture had no definite relationship with phosphorus availability. Available phosphorus at twice field capacity showed a continuous decrease in presence of organic matter and an initial decrease followed by a slight increase in absence of organic matter. However this increase was still below the initial available phosphorus level determined immediately after application.

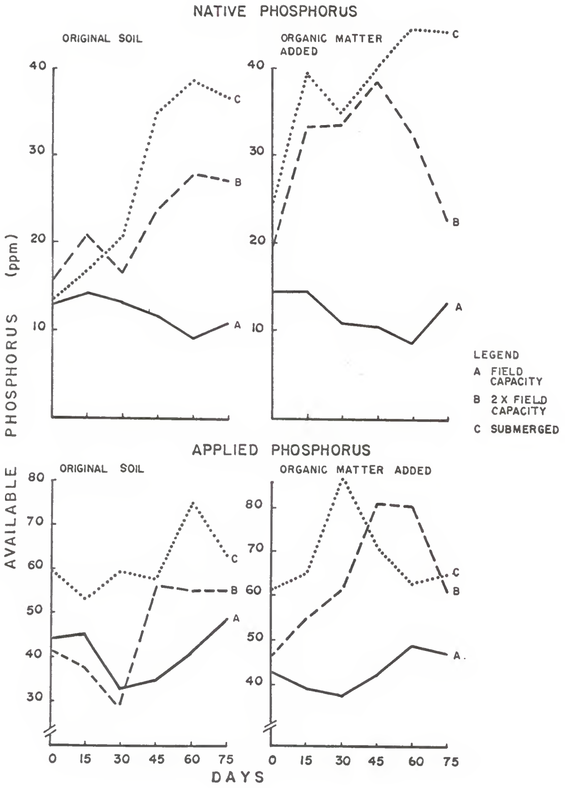

Fig. 5. CHANGES IN AVAILABILITY OF NATIVE AND APPLIED PHOSPHORUS AT DIFFERENT LEVELS OF MOISTURE AND ORGANIC MATTER IN CHEROKEE SILT LOAM SOIL.

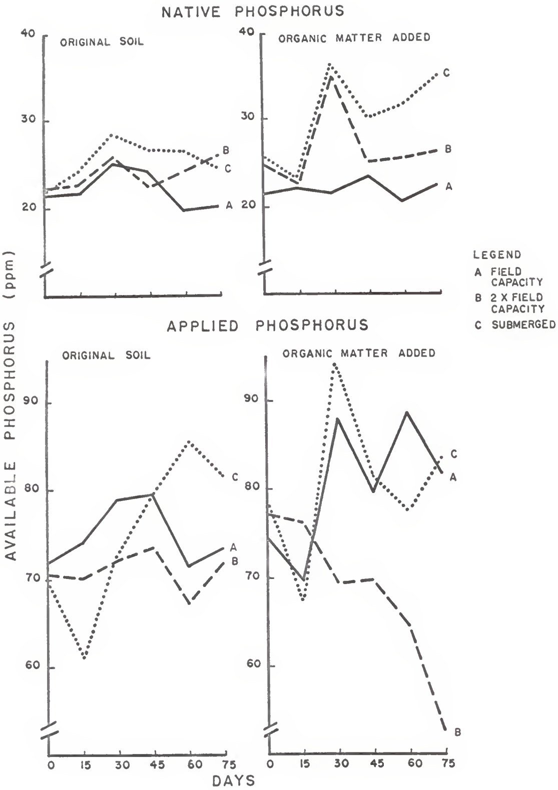

Fig. 6. CHANGES IN AVAILABILITY OF NATIVE AND APPLIED PHOSPHORUS AT DIFFERENT LEVELS OF MOISTURE AND ORGANIC MATTER IN COLBY SILT LOAM SOIL.

When organic matter was added to the Colby silt loam soil the available phosphorus curves were almost similar under field capacity and submerged conditions.

DISCUSSION

In concurrence with the findings of previous workers, Gillispie (22), Sturgis (51), Buehrer et al. (8), Yu and Li (55), Karbach (26) and many others the development of low redox potential, with an increase in soil moisture content and under submerged soils, was observed. This might be due to partial or complete displacement of oxygen from soil and rapid consumption of oxygen by soil microbes, thus resulting in a phenomenon called "anaerobiosis." Development of gases were noticed as a result of microbial activity. Under anaerobic conditions it seems that anaerobic soil micro-organisms derive their energy requirement through oxidation-reduction processes--i.e., transfer of electrons. Mineral constituents of soil like Fe, Mn, S, etc. have variable valence and are easily reduced in the absence of oxygen. The experiment supports the finding that presence of fresh organic matter in submerged soil speeds up the rate of decrease of the redox potential. In most of the treatments, where fresh organic matter was added, the greatest intensity of reduction developed within the first 15 to 20 days following submergence (Figures 3 and 4). These results agree closely with findings of many workers.

Calcareous soils usually contain less active iron ions or oxides which are involved in oxidation-reduction and phosphorus fixation. The Colby silt loam soil, being calcareous in nature, did not show similar trends in E_h values as observed in case of the Cherokee silt loam. The rise in E_h values of Colby silt loam at field capacity and initial rise up to 45 days at twice field capacity with and without organic matter, might be due to activity of OH^- ions as a result of hydrolysis of free $CaCO_3$. However the two soils showed similar trends under submerged conditions.

The availability of phosphorus was found to be markedly influenced by soil moisture and presence of fresh organic matter in soils. Under anaerobic conditions, ferric iron is reduced to ferrous state, thus increasing the relative solubility of iron phosphate existing predominately in acid soils and, consequently, increasing availability of fixed phosphorus. The results reported in Appendix II and Figure 5 show similar increases in availability of phosphorus in Cherokee silt loam soil. However, the availability of applied phosphorus in calcareous Colby silt loam, showed inconsistent results. At twice field capacity in presence of organic matter, the availability of applied phosphorus decreased. A possible explanation that can be offered for the decrease in available phosphorus, is a temporary fixation of applied phosphorus by microbial activity promoted by favorable conditions like moisture and an abundance of fresh organic matter.

In acidic soils, fixation of phosphorus through double decomposition reactions involving solubility products, is very common. These reactions are mainly due to activity of iron and aluminium ions or hydrated oxides. The changes in E_h values of acidic soils, being closely related to oxidation state of iron, have an indirect bearing on iron phosphate availability. In other words, an inverse relationship should exist between available phosphorus and redox potential values of soil. The relationships obtained between availability of native and applied phosphorus and redox potential values of soils are shown in Figures 7 and 8.

The regression lines had a negative slope indicating an inverse relationship to each other in case of Cherokee silt loam soil. The slope as indicated by regression coefficients i.e. 'b' values, was almost the same for native and

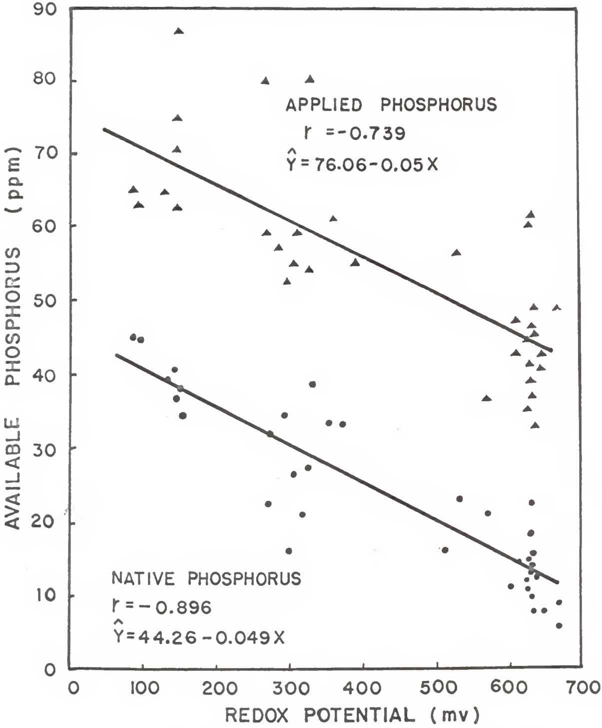

Fig. 7. RELATIONSHIP BETWEEN REDOX POTENTIAL AND AVAILABLE PHOSPHORUS IN CHEROKEE SILT LOAM SOIL.

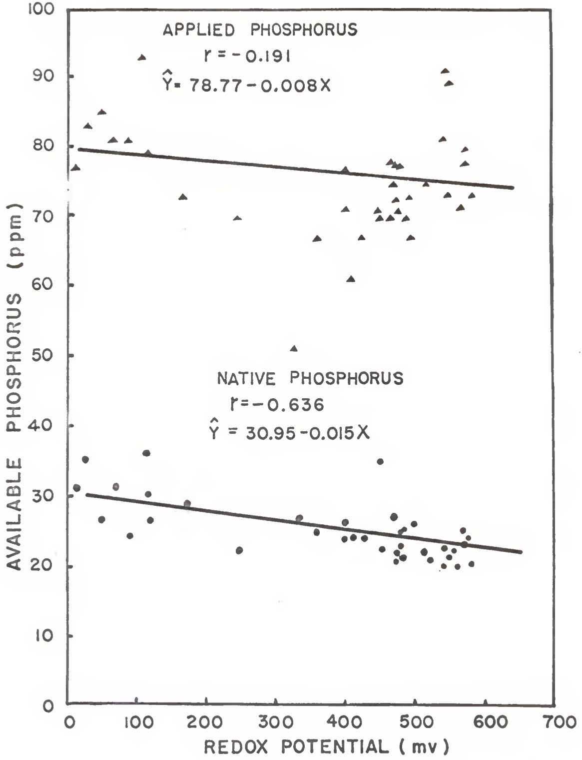

Fig. 8. RELATIONSHIP BETWEEN REDOX POTENTIAL AND AVAILABLE PHOSPHORUS IN COLBY SILT LOAM SOIL.

applied phosphorus. However, the correlation coefficients 'r' of native phosphorus and applied phosphorus were 0.896 and 0.739 respectively i.e., they were different. This indicated that the availability of native phosphorus was influenced more due to a decrease in soil redox potential than was availability of applied phosphorus. A logical explanation could be as follows:

The redox potential of soil measures the intensity of oxidation or reduction state of soil. The path of phosphorus fixation proposed by Chang and Jackson (9, 10) is:

$$\begin{array}{c}\text{Calcium}\\ \text{Phosphate}\end{array} \rightarrow \begin{array}{c}\text{Aluminium}\\ \text{Phosphate}\end{array} \rightarrow \begin{array}{c}\text{Iron}\\ \text{Phosphate}\end{array} \rightarrow \begin{array}{c}\text{Occluded}\\ \text{Phosphate}\end{array}$$

According to this proposal, under acidic conditions, native phosphorus might exist predominately as iron phosphate. Wright and Peech (52) noticed that the native phosphorus of soil, to which no phosphorus had been added, was present in the form of iron phosphate. Bhangoo and Smith (5) reported 700 lbs. of P/A as iron phosphate and aluminium phosphate out of 1090 lbs. of total phosphorus (P) per acre in the Cherokee silt loam. Now under such conditions, if reducing conditions are developed due to submergence, the existing native predominating iron phosphates would become more soluble and consequently more available. But in case of applied phosphorus fixation may not be complete. Clark and Peech (14) showed that reactions between added phosphorus and soil were not complete even after 18 months. If this is true, the present experimental period was only 75 days, hence part of the added phosphorus must have existed in forms other than iron phosphate i.e., calcium phosphate or aluminium phosphate during the 75 days experimental period. Forms like calcium phosphate or aluminium phosphate are not directly affected by a decrease in redox potential of soil. Therefore, the availability of applied phosphorus was not affected to the same extent as native phosphorus. This is shown by the correlation coefficients in Figure 7. Overall, in case of Cherokee silt loam soil, when the redox potential decreased from about 625 mv to 100 mv, the availability of native and applied phosphorus increased by 30 ppm but increase in availability of native phosphorus was more correlated to decrease in redox potential of soil.

As indicated in Figure 8, for calcareous Colby silt loam soil, the negative linear relationship was negligible in case of native phosphorus and practically absent in case of applied phosphorus. The situation can be explained on the same basis. In calcareous soil, phosphorus fixation through double decomposition reactions, involves formation of different types of calcium phosphates. It has been reported that the phosphate in calcareous soil is mainly bonded to calcium. Calcium does not change its valence and remains unaffected due to changes in redox potential of soil, hence there existed no definite relationship between availability of either native or applied phosphorus and decreasing redox potential in case of Colby silt loam soil. However, a small change in phosphorus availability with decrease in E_h value in Colby silt loam may be due to the beneficial hydrolytic effect of soil pH and microbial activity. With the addition of organic matter, the variation could be due to the chelation effect of organic matter, microbial activity and soil pH. However, it needs further investigation.

SUMMARY AND CONCLUSIONS

The available literature indicates a beneficial effect of development of reducing conditions on availability of native and applied phosphorus in soil. To study existing relationships between decreasing redox potential and available phosphorus in soil a laboratory experiment was conducted. The results for Cherokee silt loam and Colby silt loam soils indicated that:

1. On submergence of dry soil the redox potential of both soils decreased.

2. A sharp fall in redox potential was noticed, within 15 to 20 days after submergence.

3. The rate of decrease in redox potential of either soil was accelerated by presence of organic matter in the form of alfalfa hay.

4. Redox potential values reached near equilibrium conditions 75 days after submergence.

5. In general soil moisture had a beneficial effect on available phosphorus but there were some exceptions.

6. Availability of applied phosphorus showed large variations as compared to that of native phosphorus.

7. The increase in availability of soil native phosphorus appeared to be more closely correlated to the decrease in redox potential of soil than was applied phosphorus.

8. A negative linear relationship between available phosphorus and redox potential was distinct in Cherokee silt loam soil where as it was not as significant in Colby silt loam soil.

ACKNOWLEDGMENTS

The author wishes to extend grateful acknowledgment to Dr. Roscoe Ellis, Jr., his major advisor, for his valuable guidance and encouragement in course of research study. Special thanks are expressed to the Agency for International Development for providing the author an unique opportunity for higher training at Kansas State University, Manhattan, Kansas, U.S.A. Thanks are due to other faculty members of the Department of Agronomy, Kansas State University, for their cooperation in conducting the experiment.

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APPENDIX

APPENDIX I

CHANGES IN REDOX POTENTIAL OF SOILS*

Soil	Treatment		Redox potentials (mv.)					
			Days					
	Moisture	Org. matter %	0	15	30	45	60	75
Cherokee silt loam	field capacity	0	624	630	639	624	670	628
		1	627	618	635	644	669	614
	twice field capacity	0	631	565	514	528	323	307
		1	628	368	357	332	275	273
	submerged	0	631	295	316	286	150	147
		1	632	138	153	142	99	95
Colby silt loam	field capacity	0	478	519	567	575	566	583
		1	478	496	548	577	541	541
	twice field capacity	0	479	449	496	547	424	398
		1	478	401	454	483	363	334
	submerged	0	477	411	171	119	55	88
		1	476	245	112	67	14	25

* E_h values adjusted to original soil pH according to Jackson (24)
Average of two replications.

APPENDIX II

CHANGES IN AVAILABLE PHOSPHORUS IN SOILS

Soil	Treatments			Available Phosphorus* (ppm)					
	Moisture	Org. matter %	Phosphorus P lbs./A	Days 0	15	30	45	60	75
Cherokee silt loam	field capacity	0	0	12.60	14.35	13.09	11.37	8.90	10.74
		1	0	14.74	14.45	10.86	10.32	8.77	13.04
	2 x field capacity	0	0	15.94	20.99	16.17	23.45	27.69	26.51
		1	0	20.70	33.17	33.52	38.47	32.25	22.16
	submerged	0	0	13.24	16.78	21.59	34.67	38.56	36.57
		1	0	24.97	39.38	34.27	40.91	44.50	44.44
	field capacity	0	200	44.21	45.83	33.19	35.22	41.83	49.74
		1	200	43.65	39.82	37.36	42.67	49.47	47.28
	2 x field capacity	0	200	41.80	36.91	28.43	56.35	54.73	55.65
		1	200	46.52	55.52	61.51	80.51	80.12	59.50
	submerged	0	200	60.26	52.63	59.63	57.36	75.23	62.03
		1	200	62.66	64.95	87.26	70.70	63.00	65.14
Colby silt loam	field capacity	0	0	21.23	21.70	25.05	24.24	19.45	20.26
		1	0	21.44	22.33	21.77	23.67	20.17	22.51
	2 x field capacity	0	0	22.76	22.56	26.03	22.11	24.01	26.04
		1	0	25.30	22.78	35.02	25.25	25.25	26.35
	submerged	0	0	22.15	24.33	28.42	26.60	26.47	24.09
		1	0	26.78	22.89	36.43	30.95	31.63	35.71
	field capacity	0	200	72.26	74.33	79.23	79.86	71.35	73.30
		1	200	78.41	66.81	87.98	79.91	88.90	81.90
	2 x field capacity	0	200	70.68	70.17	72.77	73.48	67.31	71.79
		1	200	77.41	76.12	69.64	69.70	64.10	51.08
	submerged	0	200	69.29	61.06	72.33	79.35	85.78	81.36
		1	200	74.26	69.19	93.76	81.61	77.54	83.12

* Available phosphorus determined by Bray's method. (7) Average of two replications.

CHANGES IN REDOX POTENTIAL AND PHOSPHORUS AVAILABILITY IN SUBMERGED SOILS

by

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Rice fields, when submerged, develop reducing conditions resulting in low redox potential. The degree of development of reducing conditions is largely determined by amount of soil moisture and presence of organic matter. Availability of soil phosphorus, which is one of the limiting production factors in rice growing areas in India, shows large variations. The available literature indicates a beneficial effect on development of reducing conditions on availability of native and applied phosphorus in soil. To study existing relationships between decreasing redox potential and phosphorus availability in soil a laboratory experiment was conducted. Three soil moisture levels (field capacity, 2 x field capacity and submerged), two organic matter levels (0 and 1%) and two phosphorus levels (0 and 200 lbs P/A) were used in the present experiment. The soil pH and redox potential readings of soils were taken at 15 day intervals. Simultaneously available phosphorus by Bray's method (P-1) was determined on a separate soil sample. The results for Cherokee silt loam and Colby silt loam soils may be summarized as follows:

1) On submergence of dry soil the redox potential of both soils decreased. At field capacity E_h values were practically constant where as at twice field capacity the E_h values were intermediate.

2) A sharp fall in redox potential was noticed within 15-20 days after submergence and then E_h values showed gradual change until the end of experiment.

3) The rate of decrease in redox potential of either soil was accelerated by presence of organic matter in the form of alfalfa hay.

4) Redox potential values reached near equilibrium conditions 75 days after submergence.

5) In general increasing soil moisture had a beneficial effect on available phosphorus but there were some exceptions.

6) Availability of applied phosphorus showed large variations as compared to that of native phosphorus.

7) The increase in availability of soil native phosphorus was more closely correlated to the decrease in redox potential of soil than was applied phosphorus.

8) A negative linear relationship between available phosphorus and redox potential was distinct in Cherokee silt loam soil where as it was not as significant in Colby silt loam soil.