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## ABSTRACT

TURNER, FRED TOWNSEND. Increased Phosphorus Diffusion as an Explanation for Increased Phosphorus Availability in Flooded Rice Soils. (Under the direction of J. W. GILLIAM).

To study the P supply characteristics of alkaline rice soils, soils were selected that were representative of the neutral to alkaline Vertisols from a major rice producing area of India and an alkaline soil representative of the Mollisols of the Peruvian coast. Soils from other areas of India, North Carolina, and Louisiana were included for comparison. Adsorption of P by anion resin, measurement of the P supply factors (capacity, kinetic, intensity, and diffusivity), and evaluation of plant growth were the three approaches used to assess P supply of flooded rice soils.

Phosphorus accumulated on an anion resin in stationary contact with soil to a greater extent in water-saturated soils than in moist soils. The enhanced P accumulation in water-saturated soils was not related to the release of P during soil anaerobioses as the P accumulation occurred prior to the reduction of soil iron. The increased P accumulation in the water-saturated system was attributed to the improved P diffusion brought about by a decrease in tortuosity.

Increases in the capacity, intensity, and kinetic factors, as measured by E-value, solution P concentration, and soil P release rate to a distilled water "sink", respectively, were unpronounced and infrequent

upon water-saturation and concomitant anaerobioses. In most incidences, when increases in these three factors occurred, they were attributed to pH changes rather than anaerobioses per se. Increases in the diffusivity factor, with moisture increases from near fifteen bar to water-saturation as measured by  $^{32}\text{P}$  self-diffusion coefficients, were at least ten-fold in each soil. The greatest increases in P diffusion occurred as soil moisture increased from near one-third bar to water-saturation. Thus, these data also indicate that increased soil P availability upon flooding is a result of the increase in the diffusivity factor.

Using a P fertilized soil and a minus P nutrient solution to nourish a split root system, with rice-shoot growth and P uptake as indicators of P availability, further evidence was obtained to support the hypothesis that increased soil moisture increased P availability through an enhancement of P diffusion. When the P fertilized soil was replaced by P treated powdered cellulose, having  $^{32}\text{P}$  self-diffusion coefficients comparable to those found in soil, shoot growth and P uptake of rice plants increased with moisture of the P treated cellulose when P was a limiting factor in plant growth. In the same experimental system, no plant growth differences occurred with moisture changes when the P solution concentration was sufficiently high so that even limited diffusion could supply adequate P. In the P treated cellulose, as well as in the soil, maximum P uptake and shoot growth were obtained in the water-saturated treatment. These plant growth data are interpreted

to indicate that all the increased P availability resulting from water-saturating the cellulose was due to increased P diffusion to root surfaces.

This study does not eliminate the possibility that reduction of iron or changes in pH upon soil anaerobioses may contribute to the increase in P availability in flooded rice soils. Nor does it eliminate the possibility that rice grown under flooded conditions has a lower functional P requirement or greater P absorptive capacity. However, all three approaches employed in this study do suggest that increased P availability upon flooding is primarily due to the pronounced increase in P diffusion that occurs upon flooding.

INCREASED PHOSPHORUS DIFFUSION  
AS AN EXPLANATION FOR INCREASED PHOSPHORUS  
AVAILABILITY IN FLOODED RICE SOILS

by

FRED TOWNSEND TURNER

A thesis submitted to the Graduate Faculty of  
North Carolina State University at Raleigh  
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requirements for the Degree of  
Doctor of Philosophy

DEPARTMENT OF SOIL SCIENCE

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## BIOGRAPHY

Fred Townsend Turner was born November 2, 1941, in Beaumont, Texas. He received his elementary and secondary education in Texas and Louisiana. While at Louisiana State University obtaining a B. S. degree in Soil Science with a minor in botany and inorganic chemistry, he worked part-time as a laboratory assistant in a soil testing laboratory. Also at L. S. U. in May 1967, he received an M. S. degree in Soil Science under the direction of Dr. William H. Patrick.

After completing his M. S. study, he continued his association with Dr. Patrick for a seventeen month period during which he was involved in a laboratory and field study of the effect of soil  $O_2$  on sugar cane root development. In October 1968, he joined the Ford Foundation's Intensive Agricultural Development Program in India. During the next two years, his main input was in the Foundation's soil fertility evaluation project which employed rice as the test crop. His efforts in India laid the groundwork for his subsequent Ph. D. program which began in January 1971.

In 1967 he married DeAnna Maria Noblitt of Baton Rouge. While in India, their daughter Deborah Leigh was born in 1970.

Following completion of graduate study, he will continue his professional work at the Texas A&M University Agricultural Research and Extension Center in Beaumont, Texas.

## ACKNOWLEDGMENTS

An awareness of the importance of a Christ-controlled life has brought about a peace of mind and a sense of security in my life that has made this thesis investigation enjoyable rather than burdensome. Notwithstanding are the contributions of others to my graduate program. Sincere appreciation is extended to Dr. J. W. Gilliam, chairman of my advisory committee, for his contributions as scientist and friend toward development and completion of my graduate program. Likewise, the efforts of committee members, Drs. E. J. Kamprath, J. W. Fitts, and J. R. Troyer, along with faculty members, Drs. A. Hunter, W. A. Jackson, P. Sanchez, and S. Weed, who contributed to this investigation in an advisory role and/or through supplying facilities.

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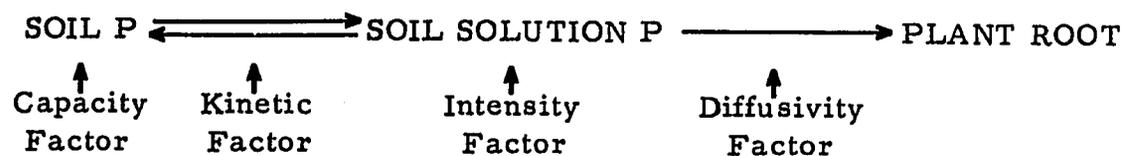
## CHAPTER I

### INTRODUCTION

Lowland rice responds inconsistently or not at all to P fertilizer when grown on the same soils in which upland crops, with P requirements similar to those of rice, respond favorably to P fertilization. The frequent lack of response to P fertilizer by lowland rice is world-wide, and the increase in P availability upon flooding is generally attributed to the release of phosphate to the soil solution from ferric phosphate compounds as iron is reduced during anaerobioses of rice soils. However, the dominant form of P in alkaline soils is likely calcium phosphate rather than ferric phosphate. The significance of P release to the soil solution during reduction of alkaline soils is unknown. In alkaline soils, it is possible that some factor other than release of P during reduction of ferric phosphate compounds is responsible for the alkaline soil's apparent adequate P supply under flooded conditions.

To study the P supply characteristics of alkaline rice soils, soils were selected that were representative of the neutral to alkaline Vertisols from a major rice belt of India (West Godavari Delta, Andhra Pradesh State) and of alkaline Mollisols from the Peruvian coast. Soils from other areas of India, North Carolina, and Louisiana were included for comparison.

Various laboratory methods, such as fractionation of soil P compounds to study P transformations, changes in extractable P due to waterlogging, and changes in water-soluble P with time after waterlogging, have been employed to characterize the increase in available P resulting from flooding a soil. A-values have also been obtained through  $^{32}\text{P}$  uptake studies with rice to show greater availability of P under flooded conditions. Likewise, P adsorption isotherms have been used to predict the P supply of aerable soils. Yet, these P characterization techniques for soils either fail to evaluate all factors in the P supply process (see diagram below) or they do not offer an explanation for the increased availability of P under flooded conditions.



In an attempt to evaluate the P supply process in lowland rice soils, this research used an anion resin to compare the P supply characteristics of moist and waterlogged alkaline soils and determined the effect of flooding on the capacity, kinetic, intensity, and diffusivity factors. These specific objectives guided the investigation.

1. To test, by laboratory techniques, the use of an anion exchange resin to characterize the P supply potential of oxidized and reduced soils.
2. To measure the effect of flooding on the capacity, kinetic, intensity, and diffusivity factors in the supply of soil P to plant roots.

3. To explain the increased P availability resulting from flooding in terms of the capacity, kinetic, intensity, and diffusivity factors.

## CHAPTER II

### REVIEW OF LITERATURE

#### Introduction

This dissertation is directly concerned with the mechanisms by which rice plants obtain sufficient soil P from alkaline soils that are P deficient for most other crops. The literature review for this subject begins with a brief survey of the nature of submerged rice soils and then considers the observed effects of flooding on P supply from soil to rice roots.

#### Nature of the Rice Soil Environment

The solid, liquid, gas, and microbial phases of an aerated soil undergo radical changes following flooding. Standing water severely restricts gaseous exchange between the atmosphere and soil. When oxygen is consumed, the microbial phase converts to an anaerobic metabolism. As a result, oxidized components of the liquid and solid phases are reduced in sequential order as determined by their affinity for electrons. These changes in the solid, liquid, gas, and microbial phases of the soil are so intricately related that the only reason for considering them separately is to simplify a description of them. More detail than is present in certain sections of this review can be obtained from these sources: Patrick and Mahapatra, 1968; Patrick and Mikkelsen, 1971; Ponnampetuma, 1955, 1965; and Sankaram, 1969.

### Gaseous Phase Characteristics

Oxygen diffusion rates in water are approximately ten thousand times slower than in air (Howeler and Bouldin, 1971). Yet, the oxygen demand of microbes in water-saturated soils is not curtailed. Consequently, oxygen concentrations in the soil can be reduced to near zero within one day after flooding, provided the soil contains an adequate energy source (Patrick and Sturges, 1955; Takai, et al., 1956; Turner and Patrick, 1968). However, restricted oxygen diffusion to the soil does not result in low oxygen concentration throughout the entire soil profile. Oxygen from the atmosphere diffusing into the standing water can oxidize the flooded soil surface to a depth of one centimeter. The actual thickness of the oxidized layer is a function of supply and biological demand for oxygen (Mortimer, 1941; Patrick and Mikkelsen, 1971; Patrick and Delaune, 1972). This oxidized surface layer supports biological processes similar to those in aerated soils. Beneath the oxidized soil surface layer, biological reduction processes result in the depletion of oxygen and the liberation of  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$ ,  $\text{H}_2$ , and even  $\text{H}_2\text{S}$  in highly reduced soils. The partial pressure of each liberated gas varies with time, microbes, and substrates. Ponnampereuma (1955) cited work by Harrison and Aiyer (1913) indicating that paddy soil contained concentrations of  $\text{CO}_2$  ranging from 1 to 20 per cent with a mean of 5 per cent. The important effect of  $\text{CO}_2$  on pH of alkaline rice soils was illustrated by Ponnampereuma, et al. (1966) and will be referred to in the section on pH.

### Biological Phase Characteristics

The excess water associated with rice soils may host appreciable amounts of algae whose photosynthetic activity release oxygen that can increase the oxygen supplied to the soil surface. This thin oxidized surface horizon supports aerobic microorganisms which function similarly to those in aerated soils. Beneath the oxidized layer, lack of oxygen suppresses the usual aerobic microbial population of bacteria, actinomycetes, and fungi and promotes the growth of anaerobic organisms. As a result of the anaerobic microbial metabolism, (1) the decomposition of organic matter is slower because less energy per unit of carbon decomposed is liberated to the anaerobes than to aerobes (Patrick and Mikkelsen, 1971); (2) the end products of decomposition are primarily  $\text{CH}_4$ ,  $\text{CO}_2$ , and organic acids (Ponnamperuma, 1955); and (3) the oxidized components of the soil's solid and liquid phases undergo reduction.

### Solid and Liquid Phase Characteristics

#### Specific Conductance

Ponnamperuma's (1965) study of specific conductance revealed that the ionic strength of soil solution increases following submergence until maximum reduction is obtained and then conductance subsides. He noted that  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  in alkaline soils and  $\text{Fe}^{++}$  in acid soils make appreciable contributions to the specific conductance of reduced soils. He suggested that these ions are present as bicarbonates or soluble hydroxides because of a high correlation between specific conductance and alkalinity.

### The pH of Solid and Liquid Phases of Reduced Soils

The pH of acid soils tends to increase to near neutrality after flooding; whereas, alkaline soils decrease in pH. This phenomenon, which helps explain chemical changes in flooded soils, was clearly defined in a report by Ponnampereuma, et al. (1966). They established that the pH of reduced acid and alkaline soils high in iron were buffered near pH 7.0 by the  $\text{Fe}_3(\text{OH})_8\text{-H}_2\text{O-CO}_2$  system. The dominating effect of  $\text{CO}_2$  on the pH of alkaline soils was established by Bradfield (1941) and Whitney and Gardner (1943). Ponnampereuma, et al. (1966) related this  $\text{CO}_2$  effect to the decrease in pH of reduced alkaline soil and showed that the pH values of reduced alkaline and calcareous soils are controlled by the partial pressure of  $\text{CO}_2$  through the  $\text{Na}_2\text{CO}_3\text{-H}_2\text{O-CO}_2$  and the  $\text{CaCO}_3\text{-H}_2\text{O-CO}_2$  buffer systems respectively.

### Oxidation-reduction Potential

Most soil scientists agree that the redox potential best differentiates a submerged soil from an oxidized one. The redox potential of a soil generally decreases rapidly initially after flooding (Ponnampereuma and Castro, 1964). The decrease is usually followed by a slight increase, then a gradual decrease until a constant minimum potential is reached, usually within two weeks. Explaining further, Ponnampereuma (1965) noted that the rate of decrease in redox potential is determined by the redox potential prior to flooding, the nature and amount of organic matter, temperature, and the characteristics and content of the oxidized components present at time of flooding. For example, the presence of

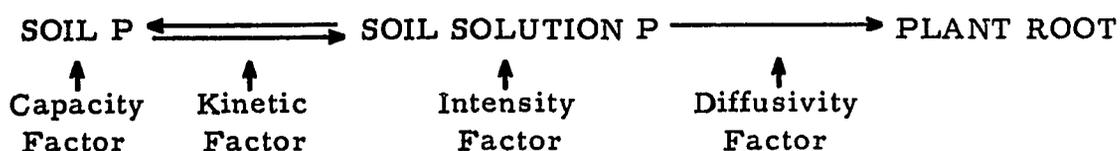
a readily decomposable substrate will accelerate the decrease in redox potential, while an abundance of nitrate exerts an appreciable restraint on soil reduction (Redman and Patrick, 1965; Bailey and Beauchamp, 1971).

#### Oxidation State of Plant Nutrients

The reduction of oxidized inorganic soil components is essentially sequential (Turner and Patrick, 1968). Oxygen disappears first at an Eh of approximately 340 mv (Turner, 1967), then nitrate and nitrite are reduced at an Eh of near 320 mv at a pH of 5.0 (Patrick, 1960). To some extent, pH influences the Eh at which oxidized compounds are reduced (Collins and Buol, 1970). Manganese reduction is especially influenced by pH (Gotoh and Patrick, 1972), but is thought to be reduced after nitrate and before iron (Patrick and Turner, 1968). Iron is reduced at about 120 mv (Patrick and Mikkelsen, 1971), and sulfate is reduced at approximately -200 mv (Connell, 1966). The cations  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ , and  $\text{NH}_4^+$  are not involved in the reduction process, although they usually increase in concentration in the soil solution due to secondary effects of submergence and reduction (i. e., solvent action of  $\text{CO}_2$  and cation exchange reactions with reduced iron and manganese). Another plant nutrient on which submergence has considerable affect is P. Numerous researchers have recognized an increase in availability of P resulting from flooding. Due to its importance in this investigation, the effects of flooding on P behavior will be the subject of another section of this literature review.

Factors in the Supply of P from Soil to Plant Roots

The following flow diagram depicting the movement of soil P from soil to plant root was originally presented by Maurice Fried and his co-workers (Fried, et al., 1957; Fried and Shapiro, 1960; Fried and Broeshart, 1967) and has been favorably received (Cook and Larsen, 1966; Gunary and Sutton, 1967; Black, 1968; Olsen and Flowerday, 1971).



This diagrammatic and segmental approach to describing the P supply process of a soil has the advantage that one can better visualize and predict the effect of various soil conditions on the over-all process of P supply from the soil to the plant root. P supply to plant roots from soils involves all four factors in the flow diagram; therefore, evaluation of only one or two of the four factors does not best describe the P supply potential of a given soil.

As Olsen and Flowerday (1971) pointed out, a near steady state equilibrium may be assumed for the P supply process. This assumption leads to the concept of the rate limiting factor in the P supply process. For example, the limiting factor determines the rate of the entire P supply process. Therefore, soil characteristics that influence either the intensity, kinetic, capacity, or diffusivity factor may have an effect on the P supply process, but the soil property that influences the rate limiting factor will have the most pronounced effect on the P supply

process. This raises the question of which factor represents the limiting factor in the P supply process of most soils?

Fried, et al. (1957) concluded that the kinetic factor was not a limiting step in the P supply process because they found that soils in their study could release P to the soil solution at least 250 times faster than the rate at which P is normally absorbed by plants. Likewise, Olsen and Watanabe (1966) established that the kinetic factor is not likely limiting by showing that soils can release P to an anion exchange resin much more rapidly than actively growing plants take up P from soils. Thus, the kinetic factor is not likely limiting; however, there is evidence that points to the capacity, intensity, and diffusivity factors as limiting the P supply process.

Fox and Kamprath (1970) used phosphate sorption isotherms for predicting P fertilizer requirements and illustrated that both the intensity and capacity factors can be low enough to limit P supply to plants. Asher and Loneragan (1967) have also shown the importance of the intensity factor in controlling P availability. Likewise, the fact that P fertilizer is required for some rice soils (Tanaka and Yoshida, 1970) to obtain maximum yields of rice is evidence that the capacity factor can limit P supply in rice soils.

The diffusivity factor as an important factor in the P supply from soil to roots has been shown by several researchers (Olsen, et al., 1962; Barber, et al., 1963; Olsen and Kemper, 1968; Olsen and Watanabe, 1971; Drew and Nye, 1970). Barber, et al., (1963) and Olsen

(1971) support the contention that diffusivity is likely the rate limiting step. They pointed out that the concentration of P in the soil solution is usually so low that root interception and mass flow of soil solution to the plant root can account for little of the P found in plants. They, therefore, concluded that the main mechanism of P transport to roots is diffusion. More recently, Folsom and Hossner (1973) noted that P diffusion accounted for 95 per cent of the P in rice plants.

From this discussion it is evident that soil properties which influence the diffusivity factor will have a pronounced affect on the phosphate supply from soil to plant roots. Changes in soil properties brought about by flooding and their effects on the four factors of the P supply characteristics will be reviewed in the following section.

#### Specific Effects of Lowland Rice Culture on the Capacity, Kinetic, Intensity, and Diffusivity Factors in the P Supply from Soil to Roots

Using the previously presented flow diagram to describe the P supply process from soil to root, one can better review the observed effects of flooding on P availability. By noting how flooding affects each factor of the P supply process, rather than merely noting the effect of flooding on various soil properties, one can gain insight into mechanisms responsible for increased P availability in flooded soils.

##### Effects on Capacity Factor

##### As Measured by A, E, and L-Values

One common method for estimating the capacity factor (the quantity of P that can be released to the soil solution) is to determine the labile

P by isotopic dilution (Olsen and Watanabe, 1963; DeDatta, et al., 1966; Olsen and Flowerday, 1971). Gunary and Sutton (1967) using short and long term uptake studies by ryegrass, established that the L-value (measure of the total quantity of plant available soil P) was a better measure of the capacity factor than E-value (measure of exchangeable soil P) or citric acid-soluble P. It appears that the only isotopic dilution technique used to characterize the P supply characteristic of rice soils has been the A-value (the availability of soil P relative to a standard fertilizer source).<sup>1</sup> However, the A-value is an ambiguous measure of the capacity factor per se, since by definition, it takes into account all four factors in the P supply process from soil to root. Nevertheless, the A-value does provide insight into the P supply process in reduced soils. Several researchers (Shapiro, 1958a, 1958b; Valencia, 1962) have shown that, with few exceptions, flooding increases A-values. At least two important points can be drawn from Shapiro's and Valencia's A-value studies with rice. (1) When calcium phosphate systems dominate the soil P fractions, flooding has less affect on the P supply from soil to root as measured by A-values (Shapiro, 1958b). (2) The P supply process from soil to root is generally increased by flooding the soils.

Valencia's 1962 A-value studies indicated that a significant portion of the increased availability of P resulting from flooding a soil is short lived. This is based on decreasing A-values with time after flooding.

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<sup>1</sup> Definitions of L, E, and A-values are from Larsen (1967).

Whereas the results of DeDatta, et al. (1966) showed little change in A-values during the first two months after transplanting. DeDatta and co-workers did not compare the A-values of moist and flooded soils but concluded that by using the A-value concept, the rice plant itself gives an indication of the P supply potential of flooded soils. Since the A-value is a collective measure of the four factors in the entire P supply process, one cannot employ the A-value as a means for explaining which factor or factors are responsible for the increased P availability upon flooding a soil. It would seem that the E-value (measure of exchangeable soil P) could best be used to specifically monitor the capacity factor during flooding and thereby ascertain the effect of flooding on the capacity factor per se. However, Talibudeen (1957) recognized that a number of conditions influence E-value determination. Those factors most pertinent to this review are these: (1) Soil solutions of low P status have very low equilibrium phosphate concentrations which lead to difficulties in chemical and radiochemical analyses; (2) When large amounts of tagged P are added to soil, it takes longer to reach isotopic equilibrium; (3) Alteration of the equilibrium pH changes the balance between the solid P and the soil solution P. Recognizing these effects, the E-value as a measure of the capacity factor offers advantages over the L-value in that the E-value can be determined quickly under laboratory conditions without the use of plants required for L-value determination.

#### As Measured by Anion Exchange Resin

Anion exchange resin, concluded Gunary and Sutton (1967), gives a good measure of the capacity factor and some measure of the intensity-kinetic complex for moist soils cropped with ryegrass. Two investigators used anion resin to assess the resin adsorbable P from reduced soil with apparently contrasting results. Davide (1960) used anion exchange resin (IRA-400, OH<sup>-</sup>) to recover <sup>32</sup>P and <sup>31</sup>P from Cecil and White store soils and found that less <sup>32</sup>P and <sup>31</sup>P were adsorbed by the resin when soils were reduced than when oxidized. Vichiensaen (1971) used anion resin sheets (111 BZL 183 Dynel-backed anion-transfer membranes) to adsorb increasing amounts of P (approximately 0.2 to 2 ppm soil P) from a Crowley soil as the Eh dropped from 200mv to -200mv. He concluded that the P supplied to the resin came from the A1-P fraction.

#### As Measured by P Fractionation

In view of the lack of data characterizing the capacity factor of reduced soils, it may be advantageous to review the efforts of various researchers to characterize the effect of flooding on soil P fractions. Numerous investigators (Davide, 1960; Basak and Bhattacharya, 1962; Valencia, 1962; Chiang, 1968; Espada, 1968; Mahapatra and Patrick, 1969; Antie, et al., 1970; Vichiensaen, 1971; Gupta, et al., 1972) have used the Chang and Jackson (1957) P fractionation scheme to detect P transformation induced by flooding. Some have criticized the fractionation scheme, but Mahapatra and Patrick (1969) were able to

distinguish accurately between added Fe and Al phosphates using the Chang and Jackson correction factor. P transformation studies have been conducted mostly on acid soils and generally have concluded that Fe-P and Al-P fractions increase (by 64 and 35 per cent respectively-- Mahapatra and Patrick, 1969) at the expense of the reductant soluble P (R. S. P.) fractions as a result of anaerobioses. The Ca-P fraction is relatively unaffected by soil reduction. However, in four acid and one alkaline Philippine rice soils, Ca-P increased during an eight week flooding period and the Al-P, Fe-P, and R. S. P. fractions tended to decrease (Islam, 1970). Equally divergent from the norm were the results of Gupta, et al. (1972) who studied a mollisol from northern India and found no apparent pattern as to the effect of flooding on P fractions. One disturbing observation concerning the P fractionation scheme is that the sum of the Fe-P, Al-P, Ca-P, and R. S. P. fractions does not remain the same as a soil changes from oxidized to reduced and vice versa. Therefore, even though one can detect increases or decreases in a given P fraction, one cannot accurately pinpoint the source of the increased P.

In summary, the effect of flooding on the capacity factor has not been established. Although the A-value supports the accepted premise that flooding increases P availability, it does not allow one to adequately define the mechanism through which flooding enhances the P supply process. Apparently it is not the anaerobic conditions that are responsible for the increased availability of P. For the anaerobic condition

is "virtually nullified" (Ponnamperuma, 1965, pg. 320), if the rhizosphere of the rice plant is oxidized and there is a considerable amount of evidence to suggest that the rice rhizosphere is oxidized (Alberda, 1953; Mitsui, 1965; Yoshida, 1966; Uemura and Moriya, 1969; Hoshino, et al., 1970). Therefore, the possibility exists that the enhanced P supply process in flooded soils may be due to some factor other than reduction because the oxidized rhizosphere should largely mask any effect of anaerobioses.

#### Effects on Kinetic Factor

Results from Olsen and Watanabe (1966) support the theory that the kinetic factor is not a limiting step in the P supply from soil to root in well drained soils. They found that an anion resin could adsorb P from a soil at a much faster rate than rapidly growing corn plants and concluded that the kinetic factor does not limit P availability. Fried, et al. (1957) arrived at the same conclusion as they showed that the formation rate of soil solution P was at least thirteen to fifteen pounds per acre per hour, which they noted was at least 250 times greater than the rate P is absorbed by one acre of plants. However, Cooke and Larsen (1966) reported that their results support the hypothesis that the kinetic factor does limit P uptake of a crop. The effect of flooding on the kinetic factor would only be speculative since there is no pertinent data for the effect of reduction on the kinetic factor.

### Effects on Intensity Factor

An increase in the intensity factor upon flooding has been attributed to the release of P during reduction of ferric phosphates (Aoki, 1941; Eriksson, 1952) and/or to the hydrolysis of Al and Fe phosphates as acid soils increase in pH upon flooding (Tanaka, et al., 1969). If the intensity factor increases due to flooding, the increase could at least partially explain the increased P availability that results from flooding a soil. Contrary to popular concepts, the intensity factor is not necessarily increased during soil anaerobioses as evidenced by the following section of the literature review.

Bartholomew (1931) apparently conducted the initial investigations into this subject using rice soils from Arkansas. He found a decrease in water-soluble P (W. S. P.) following waterlogging and attributed the decrease in W. S. P. mainly to the formation of less soluble calcium phosphates as a result of the high calcium content of irrigation water. Limnologist, Mortimer (1941) contradicted Bartholomew's observation that W. S. P. decreased on soil submergence by showing that lake muds, undergoing reduction, released P and increased the P concentration of the surrounding solution.

Mahapatra and Patrick's (1969) data indicated that waterlogging a moist soil for two months decreased the concentration of W. S. P. and loosely bound P in Midland (pH 5.8) and Crowley (pH 6.9) soils to which either Al-PO<sub>4</sub> or Ca-PO<sub>4</sub> had been added. The moisture treatment had little influence on W. S. P. when Fe-PO<sub>4</sub> was added to the two soils.

Antie, et al. (1970) waterlogged four Louisiana soils, Iberia, Sharkey, Midland, and Crowley of pH 6.3, 6.0, 5.3, and 5.2 respectively, and incubated them under oxygen or argon. Under oxygen the W. S. P. concentrations for the four soils were 0.12, 0.10, 0.23, and 0.24 ppm; whereas, in the absence of oxygen the W. S. P. concentrations were 0.25, 0.40, 0.25, and 0.25 ppm respectively. The lack of increase in the Midland and Crowley soils was attributed to their more resistant P forms. They also pointed out that the extent of P increase on waterlogging appeared to be greatest when Eh was lowest and Fe-PO<sub>4</sub> or Al-PO<sub>4</sub> concentrations were highest.

Vichiensaen (1971) reported that W. S. P. increased from 1.4 to 1.8 ppm P in a pH 5.9 Crowley soil from Arkansas as the Eh dropped from 200 to -200mv. However, Hossner and Phillips (1973) found concentrations of W. S. P. in a Crowley soil from Texas to average approximately 0.03 ppm P during the initial thirty-six days after flooding and change little with time.

Ponnamperuma (1965) followed P in the solution of four representative rice soils of the Philippines. He found essentially no change in W. S. P. of two soils; whereas, the other two soils increased in W. S. P. for twenty days and then decreased -- one reaching its initial low W. S. P. concentration after approximately forty-five days, while the other had not decreased to its original low after seventy days. Islam (1970) using Philippine rice soils also observed an initial increase in W. S. P. upon flooding, followed by a decrease after two weeks. Ponnamperuma

(1965, pg. 319) attributed the initial increase to the "reduction of ferric phosphate to the more soluble ferrous phosphate" and the displacement of P from ferric phosphate and/or aluminum phosphate by organic anions. The decrease in W. S. P. which invariably followed an increase was attributed to the resorption of phosphate on clay or aluminum hydroxide and an increase in soil pH resulting from reduction.

Although reduction of ferric phosphate is believed to result in increased P availability (Aoki, 1941; Eriksson, 1952; Islam, 1970), it may be a short lived source of available P. For example, the preceding paragraph pointed out that W. S. P. decreases when initial increases occur following waterlogging.

The results of Shapiro (1958b) support the theory that availability of both iron phosphate and aluminum phosphate decreases with increasing crystallinity. He cited Fujiwara's (1950) study which observed decreases in the availability of P when the iron and aluminum phosphates were aged.

Tanaka, et al. (1969) made a critical study of the P concentration in the solution of submerged soils and offered a realistic and pertinent conclusion regarding the reduction of ferric phosphate as a mechanism for increasing soil solution P. They pointed out that it is not logical to consider that the system controlling the P concentration in the soil solution shifts from the  $\text{FePO}_4 + \text{Fe}(\text{OH})_3$  (strengite+goethite) system to the  $\text{Fe}_3(\text{PO}_4)_2 + \text{Fe}(\text{OH})_2$  (vivianite+ferrous hydroxide) system during the development of reduced conditions, because the P released

during reduction of strengite is sorbed by the soil aluminum. Mahapatra and Patrick's (1969) data support Tanaka's theory in that they found the Al-P fraction of sixteen soils to increase by an average of 35 per cent as a result of two months of waterlogging; however, the Fe-P fraction also increased by 64 per cent -- probably at the expense of the reductant soluble P.

An increase in P concentration in the soil solution after submergence of an acid soil, concluded Tanaka, et al. (1969), is largely due to the increase in soil pH, rather than the reduction of ferric phosphate. Ponnampereuma (1955) and Patrick and Mikkelsen (1971) also offered the increase in alkalinity on submergence of an acid soil as a mechanism for increasing W. S. P. in submerged soils but presented no experimental data to support the theory.

In summary, increases in the intensity factor on reduction are not always obvious; and when increases are observed, they may be rather short lived relative to the maturation period of a rice plant. The likelihood that the intensity factor increases on soil reduction is apparently dependent on Eh, forms of P (Antie, et al., 1971), degree of change in pH (Tanaka, et al., 1969) and time after soil submergence.

It is evident from the foregoing literature review that the intensity factor is not automatically greater in reduced soils than in aerobic soils. Espada (1968, pg. 18) drew a similar conclusion in his literature review: "It appears from these results that P availability could still be a problem even under flooded conditions." From this review the author con-

cluded that factors other than reduction are more important to the increased availability of P in lowland rice soils.

Whether the intensity factor changes upon flooding becomes more relevant when one considers that an increase in the intensity factor results in an increase in the diffusivity factor. The soil properties influencing the diffusivity factor are reviewed in the following section.

#### Effects on Diffusivity Factor

The importance of the diffusion factor on P supply from soil to roots has spawned numerous investigations of the soil properties influencing P diffusion. Soil P diffusion increases with clay content (Olsen and Watanabe, 1963; Mahtab, et al., 1971) and P concentration of soil solution (Phillips, et al., 1968; Mahtab, et al., 1971), and decreases with free iron oxide content (Phillips, et al., 1968). In addition, soil moisture has been shown to be a controlling factor in P diffusion (Medershi and Wilson, 1960; Watanabe, et al., 1960; Olsen, et al., 1962, 1965; Wesley, 1965; Olsen and Watanabe, 1966, 1970; Rowell, et al., 1967; Mahtab, et al., 1971, 1972). A pronounced increase in the P diffusion coefficient occurs when soil moisture is increased. For example, Olsen, et al. (1965) showed that P diffusion coefficients increased by a factor of thirteen or more as volumetric moisture increased from approximately 18 to 47 per cent. Olsen's (1971) data revealed that as soil moisture increased from one bar to 0.05 bar, the P diffusion coefficient increased by a factor of twelve. The data of Mahtab, et al. (1971) provided evidence that, for a Miller

soil, a slight increase in soil moisture (from 32 to 39 per cent) can result in a 2.9-fold increase in P diffusion. Increased soil moisture increases P diffusion through its effect on decreasing tortuosity. Tortuosity in a given soil declines as volumetric moisture increases (Porter, et al., 1960), and as a result, P diffusion increases with moisture. Other factors such as viscosity and negative adsorption also become important in restricting P diffusion as the water content decreases (Olsen, et al., 1965). Negative adsorption describes the repulsive forces between the negatively charged clay minerals and the negatively charged P. Thus a decrease in moisture restricts P diffusion.

Mahtab, et al. (1971) illustrated the effect of applied P on P diffusion. They showed that for four soils of increasing clay content, P diffusion increased 39-, 6.1-, 5.4-, and 3.6-fold as applied P increased from 0 to 100 ppm of soil. Their results also provided evidence that as clay content of the soil increases, the effect of applied P on P diffusion decreases. These results on the effect of applied P on P diffusion are in agreement with the reports of Lewis and Quirk (1967) and Phillips, et al. (1968).

Barber, et al. (1963) illustrated by radioautographs that roots reduce the P concentration around them during P uptake. With corn as the test crop, the P concentration at the root surface was reduced by 0.65 of its original value after twenty-four hours of uptake (Olsen, 1971). Thus P diffusion to plant roots becomes important to P nutrition of a plant when the plant's nutrient demands cause a lowering of the P

concentration in the solution at the root surface. Barber, et al. (1963) indicated that such conditions often occur for P. Thus factors influencing P diffusion should influence P availability to plants. Investigations demonstrating that P availability increases with soil moisture, have been conducted at moisture tensions of one-third bar and greater (Medershi and Wilson, 1960; Watanabe, et al., 1960; Olsen, et al., 1962; Olsen and Watanabe, 1970). One-third bar tensions have been the highest moisture levels used because higher moisture levels would restrict soil aeration for aerable crops.

Mahtab, et al. (1972) demonstrated a significant relationship between soil moisture content and P uptake by sorghum plants. A graph of their data indicated that increasing the soil moisture from approximately 5 per cent to approximately 40 per cent, increased the P uptake from 5 to 18 mg P/pot respectively during a thirty day growth period. Similarly, Watanabe, et al. (1960) found that the relative uptake of P by corn seedlings was 100, 94, 80, 50, and 35 for 1/3, 1/2, 1, 3, and 9 bars soil moisture tension respectively. For a given soil, uptake of P by the corn seedlings increased linearly as soil moisture content increased.

Since increases in soil moisture cause increases in P availability, Mahtab, et al. (1972) concluded that to provide optimum P nutrition to plants, more P needs to be applied to crops during periods of moisture stress than during periods of adequate soil moisture. It follows that rice plants grown in water-saturated soils would need less applied P

than plants grown on moist soils even if the diffusivity factor were the only P availability factor influenced by moisture.

### CHAPTER III

#### GENERAL DESCRIPTION OF SOILS

The majority of soils for this study came from two rice producing regions of India. Other soils were selected from locations in Peru, Louisiana, and North Carolina. The geographic locations and general soil characteristics are summarized in Table 1.

##### Indian Soils

Soils numbered I-1 through I-5 were chosen for study because they are representative of nearly one-half million hectares of rice soil within West Godavari District, Andhra Pradesh State, India. The Godavari delta soils extend into other districts creating a major rice producing area along the eastern coast of southern India. The major catchment basin of the Godavari River is the Deccan Plateau which is covered by dark clay soils. Hence the relatively young alluvial soils of the Godavari delta represent the secondary weathered products of sub-tropical dark clay soils. The dark clay rice soils are locally known as "black soils", "black cotton soils", or "regurs". Other names have been applied to the estimated 258 million hectares (Dudal, 1965) of the dark clay soils which today are referred to as Vertisols in accordance with the Comprehensive Soil Classification System -- 7th Approximation (Srinivasan, et al., 1969). The delta soils are of the Vertisol order which dictates their high smectite clay content

(usually between 40 and 75 per cent clay -- Kumar, 1969), low organic matter accumulations, high coefficients of expansion and shrinkage, and the appearance of deep cracking during the dry season.

A series of canals stemming from the Godavari River allow rice to be grown in selected areas during the seven dry months of November through May. Most of the rice is grown during the July through October monsoon season when 80 per cent of the total 1020 mm (40 inches) of annual rainfall occurs. Average maximum and minimum daily temperatures of 28 and 18° C occur during the coolest months of November, December, and January. The warmest months of May and June average daily maximum temperatures of 35 and 25° C respectively.<sup>1</sup>

Soil number I-6 is located inland from the Godavari delta and is found on the Andhra Pradesh Agricultural University farm at Rajendranagar. It is a Vertisol, but is unique in that P fertilizer is required for it to give good rice yield.

The other Indian soil (I-7) is from Thanjavur District in the state of Tamil Nadu. This soil represents some of the soils of the Cauvery River delta, another major rice producing area. Being of the Vertisol order, its chemical and physical properties are similar to the Godavari delta Vertisols (Mosi, 1971).

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<sup>1</sup> Ten year average weather data (1959-1969) from Agricultural Research Station, Maruteru, Andhra Pradesh Agricultural University.

To provide some insight into the mineralogy of these soils, four representative soils were selected for special analyses as part of the laboratory requirements for a course in soil mineralogy. The four soils, I-4, I-6, I-7, and Pe-1 (a Peruvian soil discussed in the following section) were found to contain 1.9, 3.1, 1.5, and 1.2 per cent "free"  $\text{Fe}_2\text{O}_3$ , respectively as measured by the citrate-dithionite extraction method. This indicated that iron may be an active constituent of the alkaline soils considering the reduction and oxidation cycles to which lowland rice soils are subjected. Similarly, there appear to be considerable amounts of positively charged amorphous coatings and interlayer materials associated with the clay fraction of these soils because the CEC of I-4 clay increased from 80 to 128 meq/100 g clay when amorphous and interlayer materials were removed by heating to  $400^\circ\text{C}$  for four hours and boiling in 0.5 N NaOH for two and one-half minutes. The CEC of the I-6, I-7, and Pe-1 soils were 87, 67, and 58 meq/100 g clay, respectively (amorphous material was not removed from these three soils). The I-4, I-6, I-7, and Pe-1 soils contained 43, 36, 42, and 55 per cent clay, respectively, contained no measurable amounts of gibbsite, but contained 13, 7, 15, and 10 per cent kaolinite, respectively in the clay fraction as measured by differential thermal analysis. The major portion of the clay fraction was found to be composed of smectite clays. A calculation of structure and charge of clay minerals from total chemical analysis suggested that nontronite was the specific type of smectite clay found in soil I-4.

### Peruvian Soils

Yurimaguas and Lambayeque are the areas from which the two Peruvian soils were obtained. The soil from near Yurimaguas (Pe-2) was classified as a Typic Tropaqualf, fine-mixed, isohyperthermic and is located on the San Ramon Experiment Farm in the upper Amazon Basin. The climate reported is tropical rainforest with a mean annual temperature of 24° C and 2000 mm (79 inches) annual rainfall with no dry season. This particular sample came from the lower terraces near the Shanusi River and is representative of the soil referred to as Y-7 and adequately classified by Sanchez and Buol (1974). This Alfisol has an acid A horizon and kaolinite is the dominant clay mineral.

The soil from near Lambayeque (Pe-1) is classified as an Aridic Haplustoll, fine loamy, mixed, isohyperthermic.<sup>1</sup> It occurs on the Vista Florida Experiment Station where the climate is tropical desert with a 22° C mean annual temperature and only 200 mm (8 inches) of annual rainfall. This Mollisol has an alkaline, silty clay surface and smectite is the dominant clay mineral.

### Louisiana Soils

Two soils from Louisiana were used in various experiments. The Crowley soil (La-1) from Acadia Parish is classified as a Typic Alba-

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<sup>1</sup> Personal communication with Dr. P. A. Sanchez, North Carolina State University.

qualf, fine, montmorillonite, thermic (Westfall, et al., 1971). It is representative of the silty, poorly-drained soils commonly used for rice production in Arkansas, Louisiana, and to some extent in Texas. It is low in extractable P, yet response to P fertilizer is erratic.

The second Louisiana soil (La-2) is of the Miller series and a member of the fine, mixed, thermic family of Vertic Haplustolls (Mahtab, et al., 1971). The sample used in this study came from Red River Parish. It is not a rice soil, but is somewhat similar to the Indian soils in pH and clay mineralogy, although it is high in extractable P. Both the Crowley and Miller soils were employed by Mahapatra and Patrick (1969) in their study of P transformations in flooded soils.

#### North Carolina Soils

Two soils from North Carolina were used for comparative purposes. They were the Norfolk series (NC-1), representative of the Typic Paleudults, and the Georgeville series (NC-2), which is a member of the clayey, kaolinitic, thermic family of Typic Hapludults. Because of its high iron content and high P fertilizer applications, the Georgeville soil was selected for several laboratory studies. It was thought that reduction would have a pronounced influence on its P supply characteristics. The Norfolk soil was selected for P availability studies because of its low amount of natural P.

Table 1 follows and provides a general description of the soils selected for this study.

Table 1. Location and general characteristics of soils used in this study

Soil No.	Location	Texture	Dominant Clay Mineral	NaHCO <sub>3</sub> Extr. P (ppm)	pH	P* Recovery (%)	P Fractions (ppm)		
							Al-P	Fe-P	Ca-P
I-1	A	c	smectite	2.0	8.3	30	39	26	25
I-2	A	c	smectite	1.0	7.8	13	12	15	35
I-3	A	c	smectite	13.0	7.2	45	37	15	100
I-4	A	sic	smectite	5.0	7.0	20	40	47	106
I-5	A	c	smectite	1.0	6.2	11			
I-6	B	sicl	smectite	0.8	8.2	13	12	12	25
I-7	C	sc	smectite	4.0	5.9	30			
Pe-1	D	c	smectite	8.5	7.6	38	175	62	243
Pe-2	E	lfs	kaolinite	2.0	5.9	30	25	37	15
La-1	La.	sil	smectite		5.3		10	30	15
La-2	La.	sic	smectite		7.5		115	50	212
NC-1	N. C.	sl	kaolinite	1.0	5.0				
NC-2	N. C.	sicl	kaolinite	12.0	5.6				

A. West Godavari District, A. P. India

B. Rajendanagar, A. P. India

C. Thanjavur District, T. N. India

D. Lambayeque, Peru

E. Yurimaguas, Peru

\* measure of P fixation capacity (Waugh and Fitts, 1966)

CHAPTER IV  
MEASUREMENT AND EXPLANATION OF INCREASED  
P AVAILABILITY UPON FLOODING BASED ON STUDIES  
WITH ANION RESINS

The frequent lack of correlation between extractable P and response of rice plants to added P has been attributed to use of dry soils for analyses, while lowland rice plants absorb P from anaerobic or near anaerobic soils. Assuming an anion resin acts as a P "sink", it was felt that an anion resin in contact with a reduced soil might remove amounts of P correlated with P supply potential of an anaerobic soil. The following sections describe investigations into the increased P availability upon flooding.

**Experiment 1: Effect of anaerobic and aerobic conditions on  $\text{NaHCO}_3$  extractable and anion resin adsorbable P from four soils during a three month period**

Testing the anion resin theory discussed above and offering insight into a method for characterizing the P supply potential of reduced soils were the purposes of this experiment.

**Materials and Methods**

Two Vertisols from India (I-4 and I-6) and an acid and an alkaline Peruvian soil (Pe-1 and Pe-2, respectively) were used in this study. The I-6 soil from Rajendanagar, India is unusual in that it requires P

fertilizer to obtain high yields of lowland rice (Tanaka and Yoshida, 1970). The other three soils do not require P fertilizer for good rice yields.<sup>1</sup>

Two states of oxidation (aerobic and anaerobic) and two methods of P extraction ( $\text{NaHCO}_3$  and anion resin) dictated four treatments. For the aerobic  $\text{NaHCO}_3$  extractable P (Olsen, et al., 1954) treatment, five ml of soil were placed into a fifty ml plastic centrifuge tube, and the soil was moistened to approximately one-third bar moisture tension. The aerobic anion resin extractable P treatment was obtained by mixing one ml of anion resin (Dowex 21K, greater than 35 mesh diameter) with one ml of less than thirty-five mesh soil and slowly pouring this dry mixture into a 12 x 100 mm glass test tube as drops of water were added at a rate sufficient to obtain a moisture tension of about one-third bar. An oxidizing environment for the two aerobic treatments was created by incubating the tubes containing the moist soil in a water-saturated air environment. The air within the humid environment was renewed weekly or at sampling. Samples from all treatments were taken over a three month period as designated by the points on the curves in Figure 1.

For the anaerobic  $\text{NaHCO}_3$  extractable P treatment, five ml of soil were mixed in fifty ml plastic centrifuge tubes with six ml of water. The anaerobic anion resin extractable P treatment was obtained

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<sup>1</sup> Personal communication with Dr. P. A. Sanchez, North Carolina State University and the author's field verification trials in India.

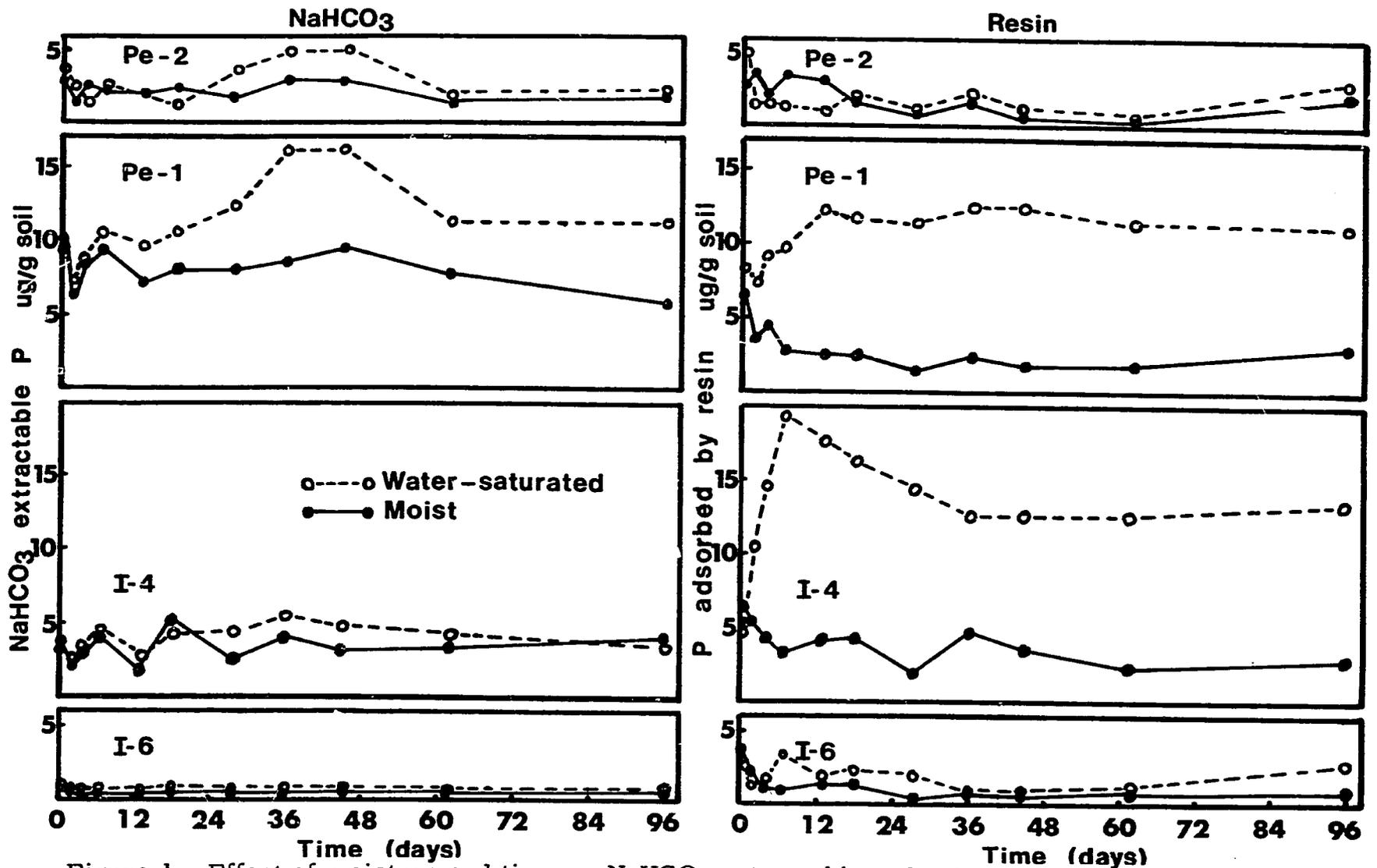


Figure 1. Effect of moisture and time on NaHCO<sub>3</sub> extractable and anion resin adsorbable P from four soils (Pe-1, Pe-2, I-4, and I-6)

by mixing one ml of anion resin (Dowex 21K, greater than 35 mesh diameter) with one ml of less than thirty-five mesh soil and pouring the mixture into a 12 x 100 mm glass test tube containing four ml of water. Anaerobic conditions for the anaerobic treatments were induced by vibrating the slurry filled tubes to remove entrapped air and then enclosing the samples in a moist nitrogen environment. The nitrogen environment was renewed weekly or after each sampling. Reducing conditions were apparent in all anaerobic treatments within one week after flooding by the darker soil color, rusty color of oxidized iron at the surface of the standing water, and the smell of the soils. Anaerobic and aerobic treatments were maintained at 30° C.

At each periodic sampling, twenty-five ml of 0.5 N NaHCO<sub>3</sub> of pH 8.5 were used to extract P from the soil of the NaHCO<sub>3</sub> extractable P treatments. For the anion resin extractable P treatments, the resin was first separated from the soil by washing the soil and resin onto a thirty-five mesh sieve with distilled water. The resin particles remained on the sieve. The P adsorbed by the one ml of anion resin while in contact with the soil was removed from the anion resin with 100 ml of 10 per cent NaCl. The solution that washed the resin was analyzed for P by the method of Watanabe and Olsen (1965).

#### Results and Discussion

From the data plotted in Figure 1, four points appear pertinent.

(1) Moisture condition of the soil had little influence on the amount of P extracted by NaHCO<sub>3</sub>, with the exception of soil Pe-1. In other

words,  $\text{NaHCO}_3$  did not detect a difference in the P supply potential of three of the soils under the two moisture regimes.

(2) The  $\text{NaHCO}_3$  extract did tend to separate the Pe-1 soil from the others in that soil Pe-1 had more  $\text{NaHCO}_3$  extractable P than the other soils. However, the  $\text{NaHCO}_3$  extract failed to detect an increased P supply in the anaerobically treated I-4 soil, whereas the anion resin procedure did.

(3) The anion resin extractable P method indicated that the I-4 and Pe-1 soils (soils which do not require P) have a greater P supply potential under flooded conditions than when just moist.

(4) The P supply potential of the Pe-2 soil and the I-6 soil (the soil that requires P), as measured by these techniques, was not increased by flooding.

The reason for not detecting an increase in the P supply power upon flooding the Pe-2 soil (a soil thought to contain adequate P for lowland rice<sup>1</sup>) is not apparent. Others (Nambiar, et al., 1973; Banerjee, 1964; Chang, 1965; Ponnampereuma, 1965; Tyner and Davide, 1962) have experienced a lack of correlation between P soil test and P availability; and Olsen (1963) has cited the need for further basic information about P availability in flooded soils before P soil tests for lowland rice can be made meaningful. The anion resin technique introduced in this study may have potential as a method for evaluating

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<sup>1</sup> Personal communication with Dr. P. A. Sanchez, North Carolina State University.

the P supply characteristic of rice soils since it could detect differences in the P supply of a flooded soil when the  $\text{NaHCO}_3$  method did not.

The release of P by ferric phosphates during soil anaerobioses is generally accepted as the mechanism responsible for increased P availability upon flooding of soils (Ponnamperuma, 1955; Patrick and Mikkelsen, 1971). Hence, the initial inclination is to attribute the increase in anion resin adsorbable P (ARAP) that occurred in this study to the release of P during reduction of ferric phosphate. However, the initial increase in ARAP appeared to occur during the first two days, probably before reducing conditions could have been established. To help establish the mechanism responsible for the increased ARAP required additional experimentation.

#### Experiment 2: Relationship between anion resin adsorbed P and ferrous iron in soils

The increase in anion resin adsorbable P (ARAP) reported in Experiment 1 for the saturated soil as compared to the moist soil, appeared to occur before iron was reduced. This indicated that the increase in ARAP under flooded conditions may have no relationship to the reduction of ferric phosphate. To identify the relationship between extractable ferrous iron and ARAP was the objective of this experiment.

### Materials and Methods

Four soils were used in this experiment (Pe-1, Pe-2, I-4, and I-6). These soils were selected to provide a range in ARAP and to have three neutral to alkaline soils and one acid soil (Pe-2). One ml of greater than thirty-five mesh, Dowex 21K anion resin was mixed with an equal volume of less than thirty-five mesh soil and poured into a 12 x 100 mm glass test tube containing four ml of water. The water saturated the soil and provided a two cm layer over the soil. Each tube was vibrated with a vortex mixer to allow trapped air to escape from the water-saturated soil. The tubes were incubated in an anaerobic environment and periodic samples were taken over a fifteen day period as illustrated in Figure 2. At sampling, the resin was separated from the soil and the resin adsorbed P determined as described in Experiment 1. Ferrous iron was extracted from the soil with  $\underline{\text{N}}$  NaOAc of pH 2.8, and measured colorimetrically by the  $\alpha$ ,  $\alpha'$  dipyridyl method (Kumada and Asami, 1958).

### Results and Discussion

From the data presented in Figure 2, two key observations were noted.

(1) In all four soils, the P accumulated on the resin before ferric compounds were reduced.

(2) After an initial rapid accumulation of P by the resin, additional adsorption of P was not evident even though substantial amounts of iron were reduced.

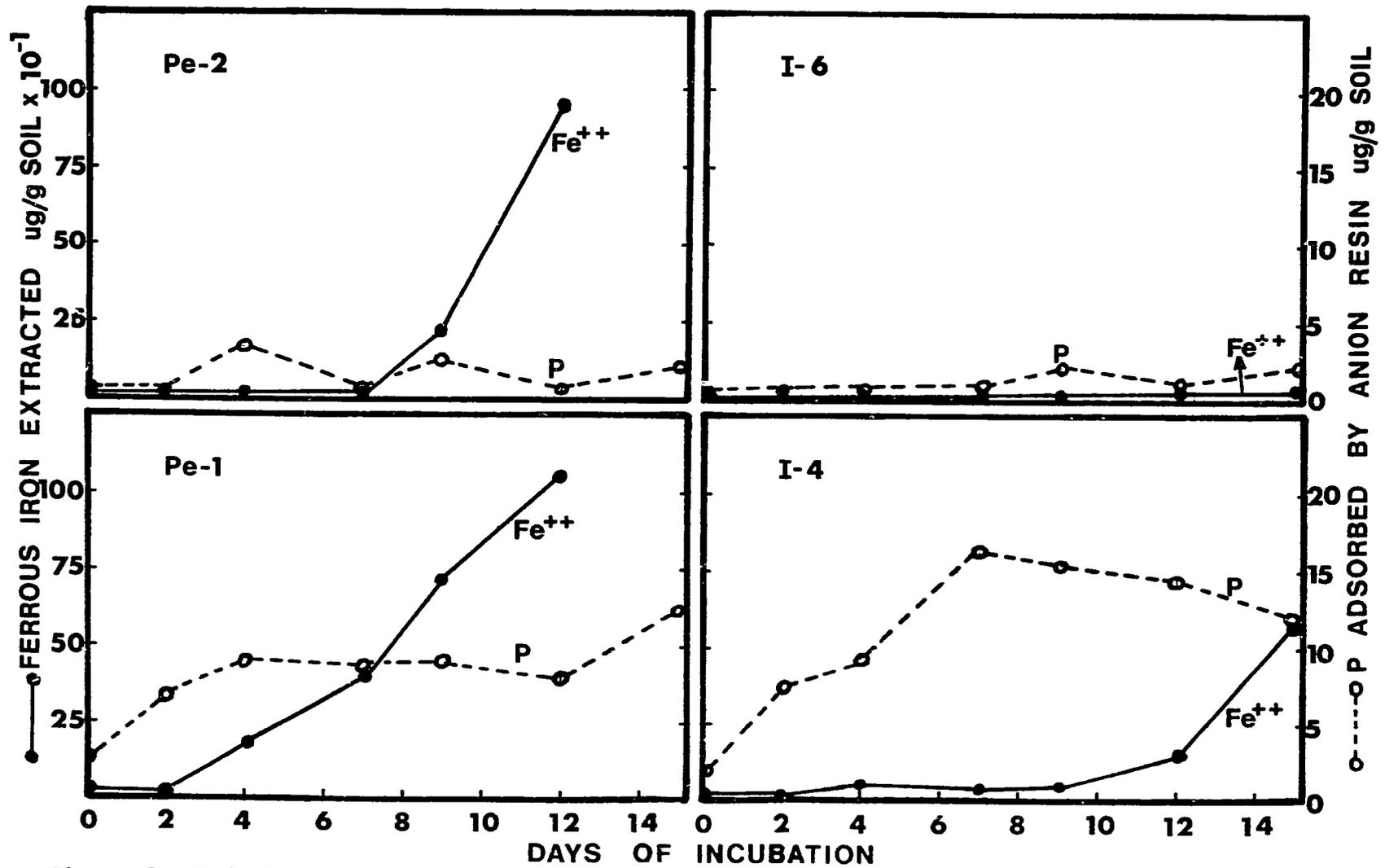


Figure 2. Relationship between anion resin adsorbable P and extractable ferrous iron with time after flooding four soils

Therefore, the results support the hypothesis that the initial rapid adsorption of P by an anion resin in a water-saturated soil, is not a result of the release of P during the reduction of ferric phosphate compounds. However, the possibility exists that the anion resin cannot adsorb P released from iron phosphate. This possibility is considered in the following experiment which makes further inquiry into how the anion resin adsorbs more P from flooded than from moist soils.

**Experiment 3: Effect of soil moisture and form of P added on the P adsorbed by an anion resin from a P deficient soil**

The objective of this experiment was to establish whether the anion resin could adsorb P from iron phosphate compounds as a soil became reduced. An additional objective was to determine the rate at which specific P compounds release P to an anion resin under water-logged and anaerobic conditions.

#### Materials and Methods

The P deficient soil used in this experiment was soil I-6 which was used in Experiments 1 and 2. It is a Vertisol from Rajendanagar, India and requires P fertilizer for acceptable rice yields. The I-6 soil was selected for this study because it has very little native resin adsorbable P. The laboratory synthesized phosphates, Al-PO<sub>4</sub>, Fe-PO<sub>4</sub>, hydroxyapatite (HAP) and dicalcium phosphate anhydrous (DCPA) contained 20.2, 29.1, 18.9, and 22.8 per cent P, respectively. They were added separately to the dry I-6 soil at 769 ug P/g soil and mixed

in a roller ball-mill. Within several days, one ml of the phosphated soil was mixed with one ml of anion resin and this mixture was poured into a 12 x 100 mm glass test tube. The moist (aerobic) and water-saturated (anaerobic) treatments were created as described in Experiment 1. Thirty tubes of soil were prepared for each P source, for example, fifteen for each moisture condition. The tubes were incubated at 30° C and individual tubes were withdrawn periodically during the forty-seven day incubation period for determination of ARAP as described in Experiment 1.

#### Results and Discussion

Only a small fraction of the added P was recovered by the anion resin (see Figure 3). This is attributed to the fact that the anion resin is not a true P "sink", the relative insolubility of the synthesized P compounds, and the soil's high P fixation capacity. Using the technique described by Waugh and Fitts (1966) for measuring P fixation characteristics of soils, only 13 per cent of added soluble P could be extracted with 0.5 N NaHCO<sub>3</sub> of pH 8.5. This recovery percentage varied very little with P applications up to 600 ppm P.

A dominant factor influencing the rate of P adsorption by an anion resin was soil moisture. The rate at which P was adsorbed by the resin was greatest in the water-saturated treatments. Water-saturation enhanced ARAP from Al-PO<sub>4</sub>, Fe-PO<sub>4</sub>, and DCPA. However, moisture had little influence on the ARAP from HAP. The lack of ARAP from the HAP treated soil is believed to be due to the relative

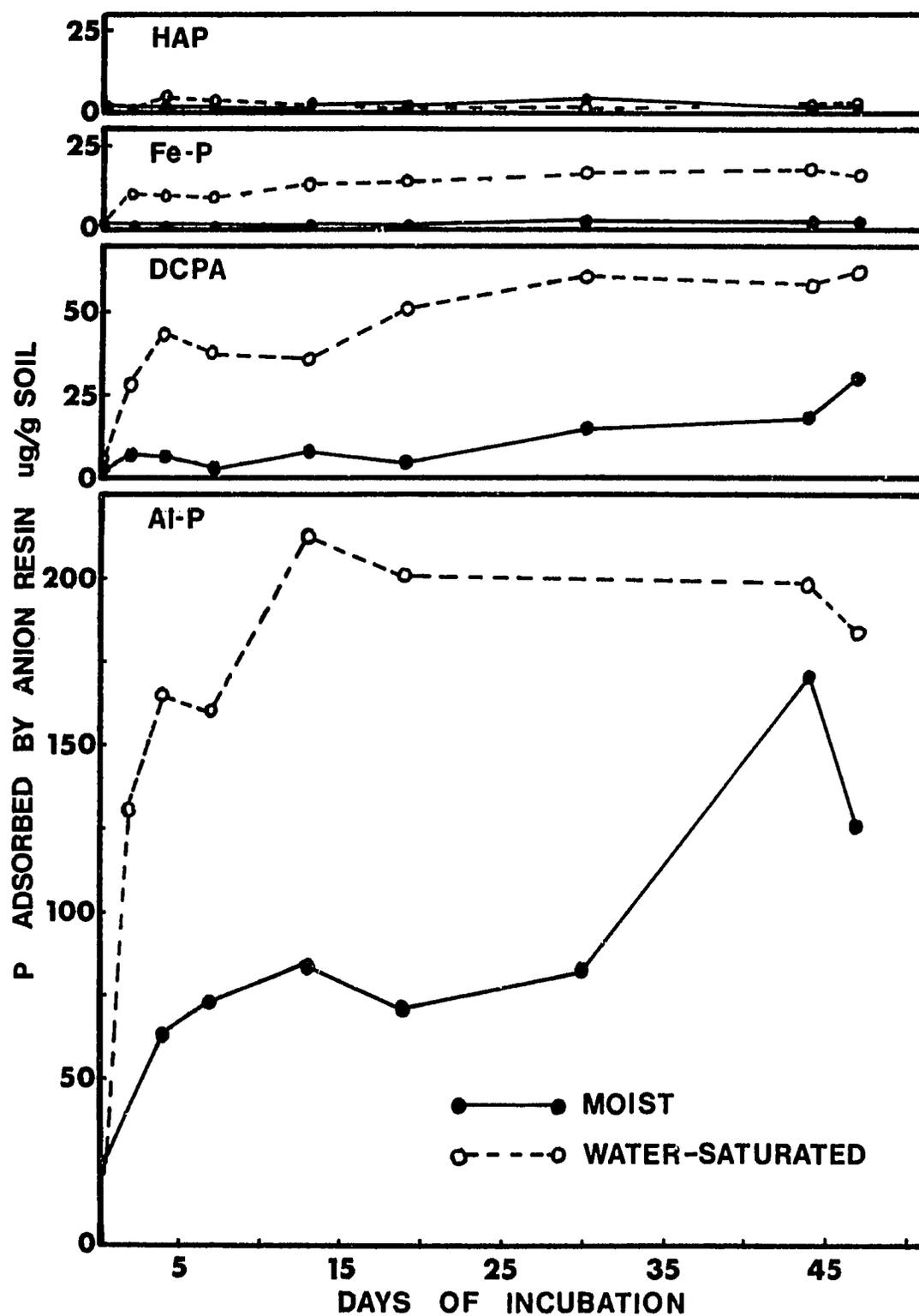


Figure 3. P adsorbed by an anion resin from a P deficient soil (I-6) to which P in the form of hydroxyapatite (HAP), iron phosphate (Fe-P), dicalcium phosphate anhydrous (DCPA), or aluminum phosphate (Al-P) had been mixed at a rate of 769 ug P/g soil

insolubility of HAP. Similarly, the greater amount of ARAP in the presence of  $\text{Al-PO}_4$  was attributed to the relatively greater solubility of the  $\text{Al-PO}_4$ .

In both the moist and saturated treatments, the P adsorption rate was initially very rapid, and the second phase of P adsorption was slower or near zero. When the second phase of the P adsorption curve is flat, it probably represents an equilibrium between soil P, added P, and resin P. If the second phase of the P adsorption curve is increasing, it suggests the release of a second, more slowly available form of P by the soil. The two sources of P theory has been postulated by various researchers and reviewed by Larsen (1967).

From the results of this experiment, it is evident that the anion resin will adsorb P from a water-saturated soil containing iron phosphate compounds. Coupling this observation with the observation from Experiment 2 that ARAP did not increase as iron compounds were reduced, suggests that P is not released during anaerobioses of these soils. Thus, one would conclude that the increase in ARAP that occurs upon waterlogging is not due to the release of P during soil reduction. It is speculated that the greater ARAP under water-saturated conditions is a result of the effect of moisture on the rate of P diffusion from soil to resin particles, rather than a release of P during reduction of ferric phosphate. Several observations support this hypothesis. First, various researchers have demonstrated that increased soil moisture can increase P diffusion by a factor of ten or more (Olsen, et al.,

1965; Mahtab, et al., 1971). Second, 50 per cent or more of the total ARAP is observed during the first forty-eight hours of incubation. During the initial period it is not likely that iron is reduced. Third, after reduction of iron is evident in Figure 2, further increases in ARAP are not noted.

Likewise, it is speculated that in the moist treatments, restricted P diffusion rather than the absence of reducing conditions, is responsible for the lower ARAP under moist conditions. Reasons why the data do not completely support the theory that enhanced P diffusion is the factor most likely responsible for the increase in ARAP upon flooding will be discussed in the summary of results of Experiments 1 through 4.

Experiment 4: Relative contributions of P diffusion and anaerobic conditions to anion resin adsorbable P in a water-saturated soil

This experiment was initiated to establish whether the greater anion resin adsorbable P (ARAP), that consistently occurs under anaerobic conditions, is a result of the effect of moisture on P diffusion or due to the effect of moisture on the oxidation status of the soil. It is important to establish the mechanism responsible for the increase in ARAP. If the reason for the greater ARAP under flooded conditions can be determined, it will offer insight into the reason for the lack of response of lowland rice to P fertilizer and thereby provide a better understanding of soil-plant relationships.

Data from previous sections of this investigation suggested that enhanced P diffusion due to water-saturation is largely responsible for the greater ARAP in flooded soils. However, the possibility that P is released during anaerobioses still exists. Therefore, this study was designed to separate the effects of water-saturation from those of anaerobic conditions on ARAP.

#### Materials and Methods

Soil I-2, because it was typical of the low labile P Indian soils, and soil Pe-1, because of its evident amount of ARAP and active iron content (Figure 2), were used in this experiment. Two parts soil, ground to pass thirty-five mesh, were mixed with one part by volume of anion resin (Dowex 21K, greater than 35 mesh diameter). Fifteen ml of the soil-resin mixture in a 250 ml Erlenmeyer flask, created a thin, level layer of soil-resin inside the flask. The following treatments were imposed, (1) moist-oxidized, (2) moist-reduced, (3) saturated-oxidized, and (4) saturated-reduced, by moistening accordingly and purging the flask with oxygen or nitrogen thereby creating oxidizing or reducing conditions independent of moisture status. Care was taken not to move the Erlenmeyer flask to prevent altering the P diffusion process within the soil-resin mixture. The samples were incubated at 30° C for periods shown in Figures 4 and 5. Individual flasks were withdrawn periodically and the contents analyzed for P and ferrous iron as described in Experiment 2.

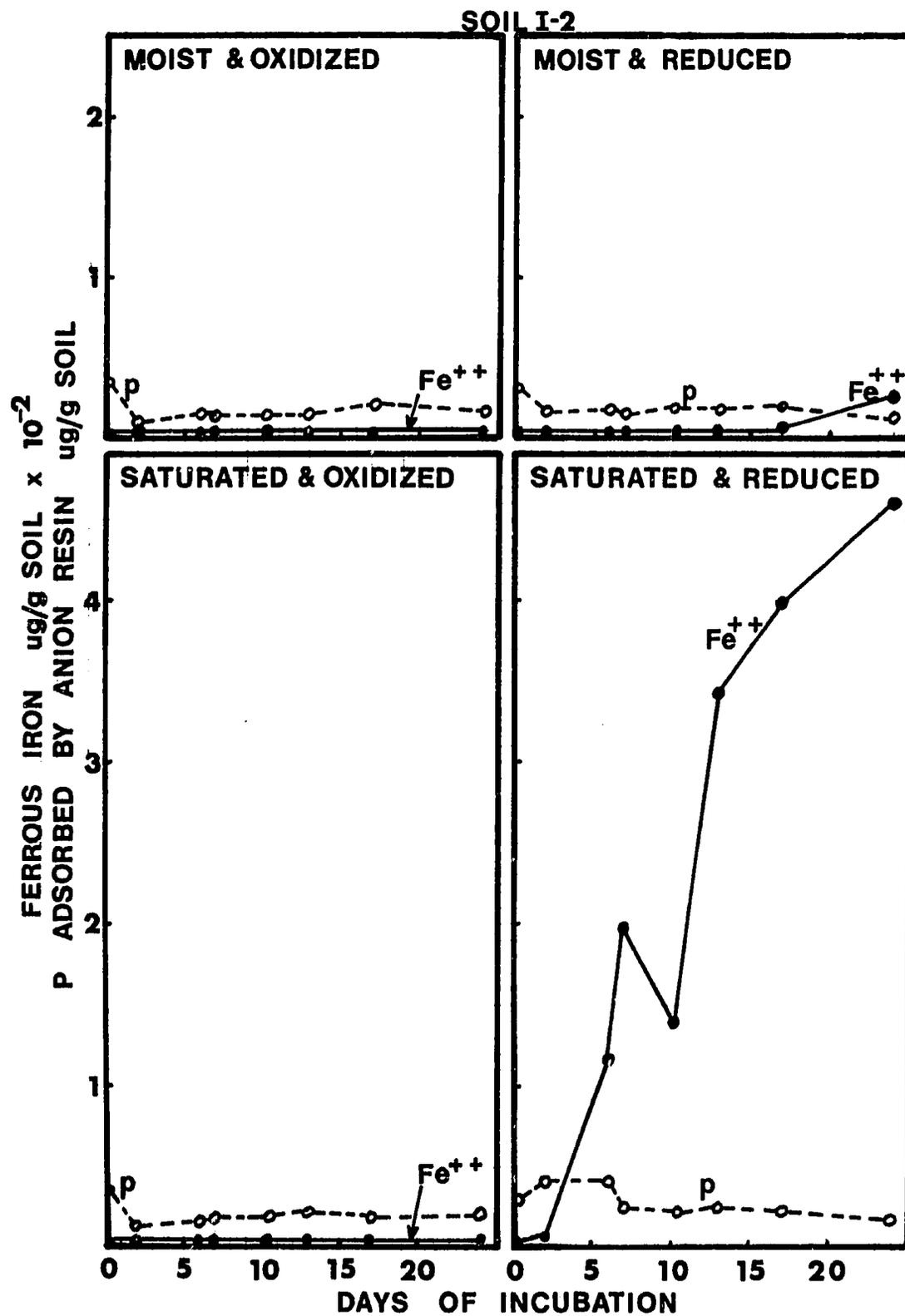


Figure 4. Effect of moisture and reducing conditions on anion resin adsorbable P and ferrous iron in soil I 2

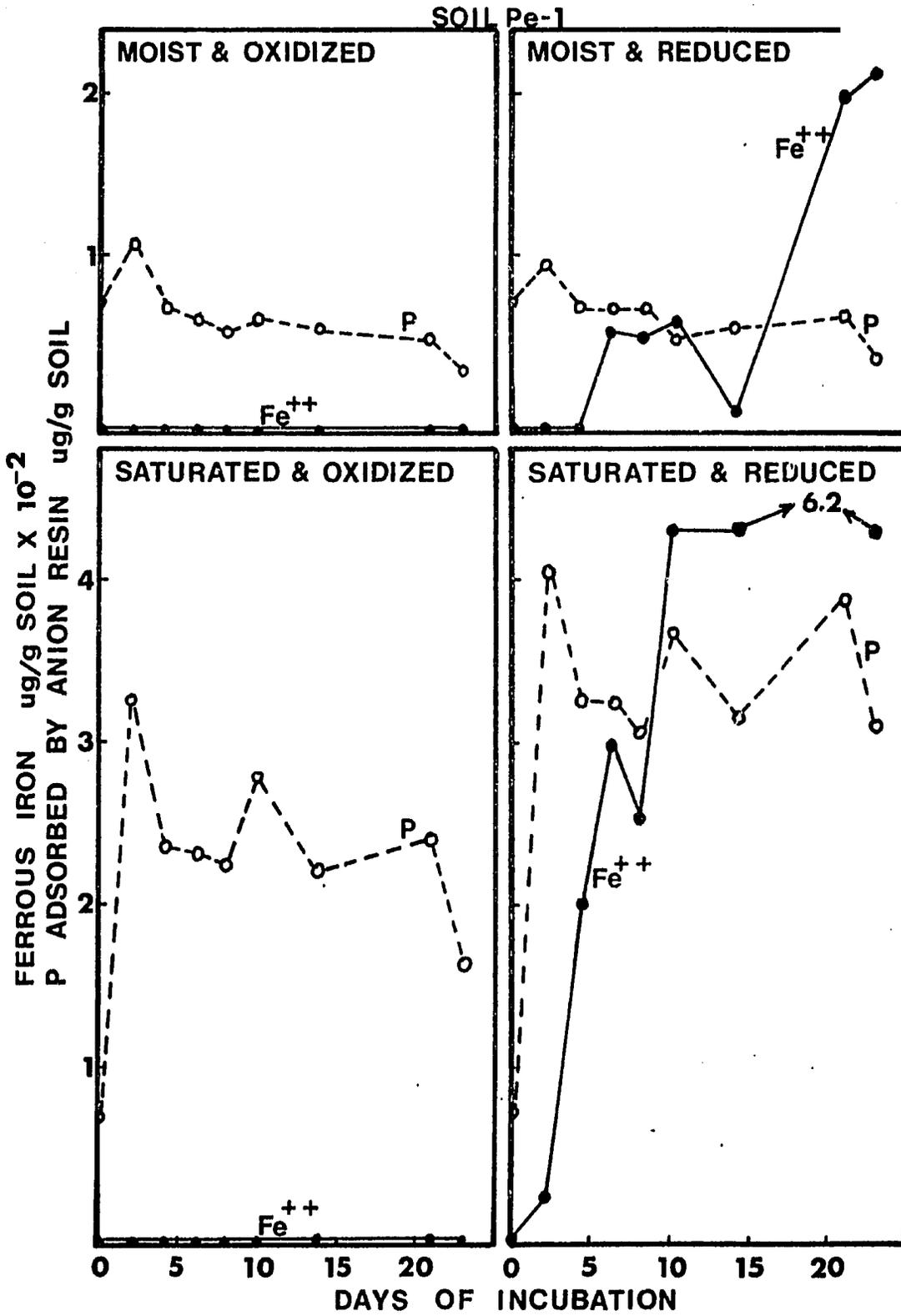


Figure 49 Effect of moisture and reducing conditions on anion resin adsorbable P and ferrous iron in soil Pe-1 in an alkaline Mollisol from Peru, Fertility-capability: Cgdc

## Results and Discussion

Neither moisture nor oxidation state had an appreciable influence on the ARAP of the I-2 soil, although slightly more ARAP was associated with the water-saturated condition regardless of the oxidation state (Figure 4). The lack of effect of moisture and oxidation state is attributed to the minimal amount of active soil P in soil I-2.

Moisture and state of oxidation had a pronounced effect on the ARAP in soil Pe-1 as illustrated in Figure 5. The water-saturated condition, possibly through its beneficial effect on P diffusion, was more of a factor in increasing ARAP than were reducing conditions. Through the average ARAP values of 0.8, 0.8, 2.5, and 3.5 ug P/g soil for the moist-oxidized (MO), moist-reduced (MR), saturated-oxidized (SO), and saturated-reduced (SR) treatments, respectively, a quantitative comparison of the effect of moisture and reduction on ARAP can be made. It is obvious from a comparison of MO (0.8 ug P) with SO (2.5 ug P), that water-saturation increased the ARAP. A comparison of MO (0.8 ug P) with MR (0.8 ug P) gives a measure of the effect of reducing conditions per se on ARAP. Reducing conditions per se had a minimal influence on ARAP as measured by this technique. However, comparison of MO (0.8 ug P) with SR (3.5 ug P) gives a measure of the combined effect of water-saturation and reducing conditions on ARAP which is an increase in ARAP of 440 per cent over the MO treatment.

The increase in ARAP in the SR treatment could be attributed to the release of P as a result of reduction in the SR treated soil. But since ARAP for the SR treatment is maximum before reducing conditions are prominent and does not increase as reducing conditions progress, it seems more reasonable to attribute the greater amount of ARAP to other factors, possibly diffusion. A decrease in the P fixation capacity of the soil during the initial stages of reduction could enhance P diffusion. Admittedly, only the surface layer of iron and manganese would have had time to be reduced, but it is the oxidized layer that reacts with P and reduces diffusion. Place, et al., (1968) have observed an increase in P diffusion with a decrease in free iron oxides. They attributed the increased P diffusion to a decrease in the P fixation capacity of soil in the absence of iron oxide. It seems logical to expect a decrease in the P fixation capacity during the initial stages of anaerobioses and therefore an increase in P diffusion as the exposed layer of oxidized iron is reduced.

It was noted that the ARAP for soil Pe-1 reached a maximum of 12 ug P/g soil in Experiment 1, Figure 1 and a maximum of 4 ug P/g soil in Experiment 4, Figure 5. The greater ARAP in Figure 1 is explained by the larger amount of anion resin per gram of soil in Figure 1. In Figure 1 the ratio of soil to anion resin was one to one, whereas in Figure 5 the ratio was two to one. The exchange capacity of the resin (3.3 meq/cc of dry resin) was not saturated with P in either case. Thus the increase in ARAP with increased soil-resin

contact adds support to the diffusion theory as an explanation for the increase in ARAP under water-saturated conditions.

An explanation is also needed for the relatively high amount of ARAP that is evident at zero time for all experiments. It represents the soil P that accumulated on the anion resin as water was used to wash the soil from the anion resin. The resin was collected on a thirty-five mesh sieve.

In summary, water-saturation, through enhancement of P diffusion, is thought to be mainly responsible for the increased ARAP in the flooded soils of this study. Reducing conditions can conceivably contribute to increased ARAP in flooded soil through improving conditions for soil P diffusion as a result of a decrease in the P fixation capacity upon soil anaerobioses. It is recognized that the effect of reduction on diffusion is probably greater in soils in which oxidized iron and manganese represent the major mechanisms for P fixation. In such soils, soil P may be desorbed upon reduction. When calcium is the predominant P fixer, reduction presumably would have less effect on P diffusion and thus on ARAP. Shapiro (1958b) and Mahapatra and Patrick (1968) have observed that the calcium phosphate fraction was relatively unchanged by flooding. The influence of moisture on P diffusion as a result of decreased tortuosity would be evident in both acid and calcareous soils.

### Summary of Results and Discussion of Experiments with Anion Resins

Ponnamperuma (1965, pg. 475) enumerated the factors responsible for the lack of quantitative correlations between soil test and P fertilizer response by rice. A recent recognition of the need for re-evaluation of soil testing methods and the P fertilizer requirements of rice soils is by Nambiar, et al. (1973). Their investigation employed some of the same Indian soils utilized in this study. Laboratory experiments from this investigation indicated that anion resin adsorbed phosphorus (ARAP) has potential for characterizing the P supply potential of rice soils. Lathwell, et al. (1950), Amer, et al. (1955), Sheard and Caldwell, (1955), Moser, et al. (1959), and Cooke and Hislop (1962) have all demonstrated the adequacy of anion resin for measuring the soil P availability for aerable crops. The resin technique employed here, to assess the P supply potential of rice soils, requires stationary contact between soil and resin, thereby allowing soil P diffusion rates to influence the quantity of P adsorbed by the resin. That P diffusion is the mechanism by which P is transported to root surfaces (Barber, et al., 1963; Olsen, et al., 1962; Folsom and Hossner, 1973) makes this anion resin method particularly effective for evaluating the P supply of lowland rice soils. It is realized that field evaluation of the relationship between rice yield and ARAP would be necessary for proper evaluation of the suggested anion resin technique for assessing the P supply potential of lowland rice soils. The primary point is that the suggested resin technique may have potential as a soil test

method for rice soils and does have application as a research tool for evaluating the P supply characteristics of rice soils.

Considerable experimentation was undertaken in an effort to explain increased ARAP upon water-saturation of the soil. It was felt necessary to establish the reason for the greater ARAP under flooded conditions because to do so might offer insight into the increased availability of P in waterlogged soils. The three mechanisms which have been proposed to explain the increased P availability of flooded soils are evidence of the universal nature of the phenomenon, yet there is lack of agreement about the cause (Patrick, et al., 1973). Based on data of this study, increased P diffusion upon flooding is offered to explain the majority of the increase in ARAP upon flooding and is also proposed as a fourth mechanism, hitherto not considered, for increasing P availability in lowland rice soils.

Unfortunately, the ARAP curves in Figures 1, 3, and 5 do not perfectly follow the diffusion theory hypothesis. Ideally the ARAP curve for the water-saturated soil should reach a maximum plateau, assuming that an equilibrium is established in the water-soil-resin system and all P diffusion factors, such as solution P concentration, remain constant during incubation. Also the ARAP curve for the moist soil should increase steadily, eventually reaching the same plateau attained by the ARAP curve for the water-saturated soil. The ARAP curves in Figures 1, 3, and 5 are not totally in harmony with the diffusion theory. For example, the ARAP curves for the moist

soils do not increase gradually as they theoretically should. The following two points are offered as partial explanation for the failure of the ARAP curves for the moist soils to approach those of the water-saturated soils: (1) The anion resin is not a perfect P "sink", (2) Drying a soil causes an increase in water-soluble P (W. S. P.) and extractable P (Savant, et al., 1970) which decrease with time after moistening the soil. The decrease in W. S. P. concentration with time would reduce P diffusion (Olsen, et al., 1961; Vaidyanathan and Nye, 1970; Mahtab, et al., 1971) resulting in a reduced rate of P accumulation on the resin or even a loss of P from the resin if the soil solution P concentration gets low enough. In Figure 3, where P was added and conceivably increased the soil solution P concentration, the ARAP curves for the moist soils treated with  $\text{Al-PO}_4$  and DCPA did tend to increase with time, even though it is evident the data do not perfectly support the diffusion hypothesis as an explanation for the increased ARAP under flooded conditions. It is recognized that factors other than moisture (lack of perfect P "sink" and changes in P concentration of soil solution) were influencing P diffusion and ARAP.

Results from the experiments with anion resins show that there was no increase in ARAP as iron became reduced. There was an increase in ARAP under waterlogged conditions when iron phosphate was added to soil, but the increase occurred before reducing conditions were evident; as reducing conditions became more evident, no increase in ARAP was observed. Reasons for not detecting an increase

in ARAP as the soil was reduced could be due to, (1) lack of reductant-soluble soil P, (2) soil solution P being controlled by the calcium system so that P released during reduction had little effect on solution P concentration, or (3) inability of the anion resin to measure the increase in "available" P attributed to soil reduction. The third possibility does not seem likely because the anion resin could adsorb P in the presence of iron in a water-saturated soil as seen in Figure 3.

It is proposed that water-saturation through an enhancement of P diffusion is responsible for a major portion of the increased P availability resulting from flooding an alkaline soil and very likely responsible for much of the increased P availability upon flooding an acid soil. Four observations support the P diffusion hypothesis as a mechanism for the increased ARAP and P availability upon flooding a soil.

(1) Increased soil moisture always increased ARAP when the soil had the capacity to supply P, even when the increased soil moisture did not induce anaerobioses. Thus, the increased ARAP was apparently a result of water-saturation per se rather than the reducing conditions usually associated with a water-saturated soil system.

(2) It was shown experimentally that the anion resin could adsorb P released from ferric phosphate mixed with a soil. Yet, ARAP did not increase after reducing conditions became evident by the increase in extractable ferrous iron. Therefore, it was concluded that the

release of soil P during soil reduction was not responsible for the increased ARAP upon flooding a soil.

(3) Various researchers have noted the oxidized rhizosphere of rice roots even though the roots penetrate a reduced environment (Alberda, 1953; Mitsui, 1965; Yoshida, 1966; Uemura and Moriya, 1969; Hoshina, et al., 1970). Assuming the rhizosphere is oxidized, then the influence of reduction toward increasing soil P availability would be masked by the oxidized rhizosphere of the rice plant. Ponnampereuma (1965) pointed this out earlier by noting that increased P availability caused by reduction should be virtually nullified by the oxidized rhizosphere.

(4) Olsen, et al. (1961, 1962, 1963), Wesley (1965), and Mahtab, et al. (1972) have shown that increasing soil moisture to one-third bar moisture tension increased P availability by increasing P diffusion. Data presented here suggest that soil P diffusion is maximum in water-saturated conditions. Therefore, P availability should be at its maximum in flooded soils. Mahtab, et al. (1971) support this point as they concluded from their data that more P would have to be applied to soils during periods of moisture stress than during more normal growth periods in order to provide optimum P nutrition to plants. It follows that less P is required in water-saturated rice soils, where P diffusion is maximum, to maintain optimum P nutrition.

## CHAPTER V

EXPLANATION OF INCREASED P AVAILABILITY UPON FLOODING  
A SOIL: THE EFFECT OF FLOODING ON THE CAPACITY, KINETIC,  
INTENSITY, AND DIFFUSIVITY FACTORS, AND PLANT GROWTH

The forethought instigating this series of experiments was that by monitoring the capacity, kinetic, intensity, and diffusivity factors as a soil was flooded, one could possibly explain the increase in P availability in flooded soils based on changes in one or more of these factors. Subsequently, it was felt necessary to use plant parameters to verify the initial results. The following sections describe the techniques and results of each experiment. The final section provides a summary of experimental results and conclusions.

Experiment 5: Effect of moist and flooded conditions on the capacity factor

The E-value (quantity of soil P exchangeable with  $^{32}\text{P}$ ) has been shown by Gunary and Sutton (1967) to be a reliable indicator of the capacity factor. In addition, the E-value can be determined rather quickly in the laboratory. For these reasons the E-value was employed to characterize the capacity factor under moist and waterlogged conditions in an attempt to determine whether an increase in the capacity factor upon flooding a soil could explain the increased availability of P in lowland rice soils.

## Materials and Methods

Five ml of each soil, containing 0.5 per cent finely-ground, dried grass to encourage anaerobic conditions, were either moistened or waterlogged with 0.01 M CaCl<sub>2</sub>. Duplicated samples were incubated at 30° C in unstoppered 100 ml plastic centrifuge tubes for periods of one, three, seven, and eleven weeks. Eh and pH were measured just prior to E-value determination. The E-value determination began with a twenty-four hour equilibration period during which the moist and waterlogged soils, still in the centrifuge tubes, were shaken with fifty ml of 0.01 M CaCl<sub>2</sub> spiked with eight to twenty uc of carrier-free <sup>32</sup>P. To prevent oxidation of the waterlogged soils during the equilibration period, the gas in the stoppered centrifuge tube was purged with nitrogen after adding the <sup>32</sup>P. Upon completion of the <sup>32</sup>P:soil equilibration period, one ml of Superfloc-127 (1 g/200 ml H<sub>2</sub>O) was added to the suspension before centrifuging. One ml aliquots were then taken from the supernatant and added to ten ml of scintillation fluid which had been prepared by dissolving 0.5 g of Dimethyl POPOP and 15 g of 2,5-Diphenylozazole in two liters of toluene and mixing with one liter of Triton X-100. A liquid scintillation counter was used to assay the one ml aliquot for <sup>32</sup>P. Twenty ml aliquots were taken from the supernatant for colorimetric P analysis. The E-value was then determined from the equation used by Amarasiri and Olsen (1973):

$$\text{E-value or labile P} = \frac{\text{P in solution}}{\frac{^{32}\text{P remaining in solution}}{^{32}\text{P added}}}$$

The precise amount of  $^{32}\text{P}$  added was determined by following the same assay procedure as previously described, but without soil in the centrifuge tube.

### Results and Discussion

The recorded Eh and pH values of the moist soils were typical of oxidized soils, but the measured Eh values for the waterlogged samples were not as low as expected (Table 2). However, reducing conditions in the waterlogged samples were evident by the decrease in pH of alkaline soils and increase in pH of acid soils. Their darker color and their ring of oxidized iron near the top of the centrifuge tube provided further evidence that the waterlogged samples were reduced.

The reduced condition consistently produced a greater capacity factor in the La-2 and I-3 soils during the incubation period. For the other eight soils of this study, oxidation state had little measurable influence on their capacity factor or the influence varied with time (Figure 6). In looking at the data critically to explain why soils La-2 and I-3 had greater E-values when reduced, it was noted that the flooded treatments consistently had approximately one-half unit lower pH values than the moist treatments (Table 2). Since these soils are calcareous (they effervesce in acid), the lower pH could result in an

Table 2. Eh, pH, E-values, and solution P concentration in ten moist and water-saturated soils at 1, 3, 7, and 11 weeks incubation

Soil No.	Incubation Time																
	One Week				Three Weeks				Seven Weeks				Eleven Weeks				
	Sol. P (ug/ml)	pH	Eh (mv)	E-value **	Sol. P (ug/ml)	pH	Eh (mv)	E-value **	Sol. P (ug/ml)	pH	Eh (mv)	E-value **	Sol. P (ug/ml)	pH	Eh (mv)	E-value **	
I-1	m*	.005	8.0	480	0.7	.007	7.9	500	7.0	.008	8.0	460	6.0	.012	7.9	500	7.0
	w*	.008	7.3	310	0.9	.008	7.2	150	1.0	.007	6.9	140	2.0	.010	7.3	210	3.0
I-3	m	.061	7.1	530	25.0	.063	7.3	590	15.0	.073	7.3	460	25.0	.085	7.6	490	33.0
	w	.068	6.8	330	28.0	.063	6.7	310	35.0	.050	6.8	110	39.0	.051	7.0	140	60.0
I-4	m	.017	6.8	500	6.0	.014	6.9	540	2.0	.010	7.1	460	5.0	.018	7.0	520	40.0
	w	.016	6.8	210	17.0	.014	6.9	290	8.0	.016	6.6	210	7.0	.017	6.9	150	21.0
I-5	m	.003	5.6	510	0.1	.007	5.6	530	0.9	.002	5.3	440	2.0	.003	5.6	540	2.0
	w	.002	5.9	320	0.3	.008	5.9	200	0.9	.005	5.3	190	5.0	.006	6.3	220	0.5
I-6	m	.004	7.8	400	0.3	.005	7.7	500	0.3	.003	7.5	400	1.0	.003	7.7	480	1.0
	w	.005	7.4	340	0.3	.005	7.3	220	0.3	.006	6.9	220	2.0	.007	7.1	260	1.0
I-7	m	.003	5.9	530	0.3	.003	5.9	540	0.4	.003	5.9	450	3.0	.006	5.9	410	9.0
	w	.005	6.1	140	0.4	.010	6.2	160	0.9	.015	6.1	170	2.0	.013	6.4	280	0.6
Pe-1	m	.025	7.6	500	21.0	.032	7.6	540	9.0	.030	7.5	470	81.0	.034	7.6	500	55.0
	w	.028	6.8	170	14.0	.034	6.8	140	11.0	.024	6.8	140	76.0	.028	7.1	220	40.0
La-1	m	.001	5.5	460	0.5	.004	5.1	600	0.7	.005	4.6	470	3.0	.005	5.1	600	3.0
	w	.004	6.6	100	0.3	.010	6.6	100	0.6	.013	6.3	150	2.0	.010	6.4	150	0.9
La-2	m	.107	7.7	380	35.0	.126	7.6	570	18.0	.071	7.0	430	50.0	.069	7.1	490	36.0
	w	.230	7.1	180	55.0	.123	7.1	100	28.0	.109	6.8	130	95.0	.034	6.9	140	54.0
NC-2	m	.004	5.5	750	4.0	.010	5.5	810	0.8	.009	4.8	510	25.0	.007	5.3	550	36.0
	w	.007	6.1	360	0.5	.012	6.1	390	5.0	.015	6.2	140	2.0	.010	6.6	300	1.6

\* Soil moisture treatment: m = moist, w = water-saturated.

\*\* E-value units = ug P/g soil.

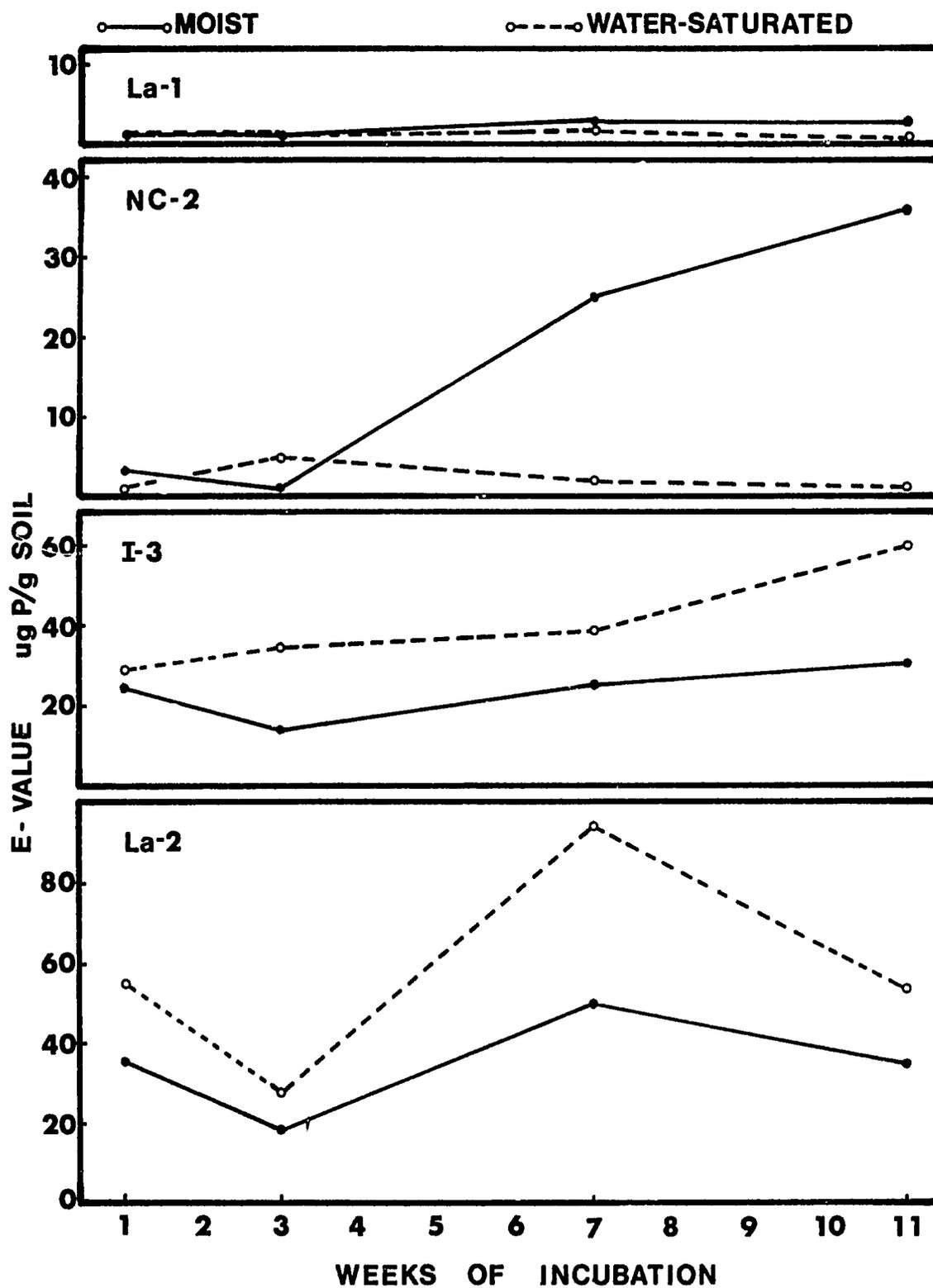


Figure 6. Comparison of E-values (capacity factor) in soils under moist (aerobic) and water-saturated (anaerobic) conditions. (Continued next page)

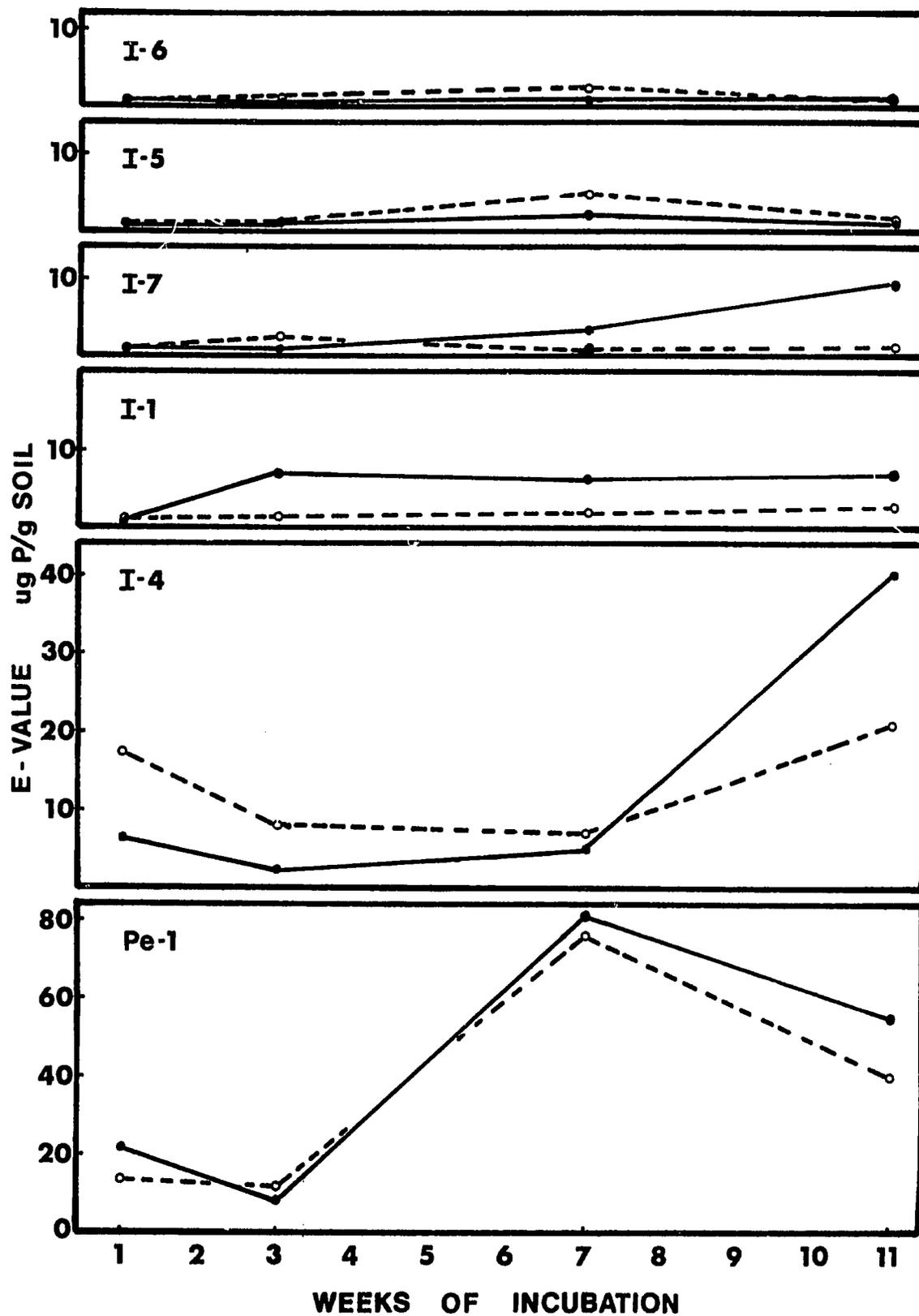


Figure 6. (Continued)

increase in isotopic exchange of the native calcium phosphate, thereby increasing the capacity factor of soils La-2 and I-3. Similarly, Tanaka, et al. (1969) have concluded that the higher P supply power of submerged soils, compared to upland soils, is due mainly to pH changes that occur upon flooding. However, this hypothesis, that the increase in E-value is a result of a decrease in pH, is not supported by soils I-1, I-6, and Pe-1. This illustrates that pH is not the only factor influencing E-values.

According to other reports (Ponnamperuma, 1955; Davide, 1958; Patrick, 1964; Broeshart, et al., 1965; Patrick, et al., 1973; Singlachar and Samaniego, 1973), reductant soluble P (R. S. P.) becomes a source of P to rice plants grown in reduced soils. If R. S. P. becomes available to rice plants, it appears that R. S. P. would become more isotopically exchangeable as reducing conditions are imposed and thereby very significantly increase the E-value or capacity factor. Since in this study, increases in the capacity factor in eight of ten soils were not related to reducing conditions, it appears that there is no difference between the isotopically exchangeable R. S. P. under oxidized and reduced conditions when both were allowed to equilibrate with the  $^{32}\text{P}$  for twenty-four hours. Shorter equilibration periods may allow detection of differences in isotopic exchangeability of R. S. P. under reduced conditions as opposed to oxidized conditions. A shorter equilibration period may have produced larger E-values under reduced conditions than under oxidized conditions.

The variation in E-values with time was somewhat unexpected because by definition the E-value represents a specific amount of P. However, as expected, higher E-values were found in the soils with greater amounts of labile P. In this light, some of the variation in E-values with time may represent the dynamic nature of the isotopically exchangeable P. This dynamic nature points out the problems of obtaining one E-value and trying to correlate it with P uptake and crop yield that occur over a period of several months. The important point gained from this study is that waterlogging resulted in consistently higher E-values in only two of the ten soils studied. In the other eight soils, waterlogging had little influence or the influence varied with time after flooding.

#### Experiment 6: Effect of flooded conditions on the kinetic factor

The kinetic factor, one of four factors in the P supply from soil to plant roots, is the rate at which soil P replenishes the soil solution. Fried, et al. (1957) and Olsen and Watanabe (1966) have shown that the kinetic factor is not a limiting step in the P supply from soil to root in well drained soils. It was not anticipated that the kinetic factor was limiting in flooded soils, but it was felt necessary to evaluate the influence of flooded (anaerobic) conditions on the kinetic factor.

#### Materials and Methods

To compare the kinetic factor of anaerobic and aerobic soils, it was necessary to devise a satisfactory means for measuring the rate

of release of soil P. Several methods employing anion resin were tested for their potential to measure the kinetic factor and were rejected because the resin was not a true P "sink". The method utilized was based on the assumption that soil solution P would diffuse freely across a dialyzer membrane to a P "sink". The P "sink" was distilled water that was renewed frequently. The actual apparatus consisted of a plexiglass cylinder ( $l = 24$  cm,  $r = 2$  cm) which enclosed a dialyzer tube ( $l = 24$  cm,  $r = 0.9$  cm when inflated). This tube-cylinder arrangement created two compartments separated by the dialyzer membrane. The compartment encompassed by the dialyzer tube was filled with 75 ml of distilled water. The volume outside the dialyzer tube contained 100 g soil mixed with 250 ml of water. Thus, the dialyzer tube served as a semi-permeable membrane separating the soil particles from the distilled water. Sample ports for each compartment projected through rubber stoppers at each end of the plexiglass cylinder to allow renewal of the distilled water and sampling of the soil:water suspension.

Prior to actual sampling, a seven day period was imposed to establish oxidized and reduced treatments for each soil. Oxidizing conditions were maintained by periodically purging the soil in the cylinder with oxygen. Anaerobic conditions were obtained by adding 0.05 g sucrose to the soil and purging both compartments of the cylinder with nitrogen. The nature of the compartments of the cylinder were such that some sucrose was removed as each distilled water sample was removed.

Additional sucrose was added during the sampling period if the intensity of the anaerobic conditions decreased. Later it was necessary to produce an oxidized treatment with a soil pH adjusted to that of the reduced soil. The pH was adjusted with dilute sodium hydroxide or hydrochloric acid.

During the actual experimental period, each cylinder was shaken to minimize P diffusion with the soil:water suspension as a factor in the release of P from soil to the distilled water. Every four hours, samples of the soil:water suspension were withdrawn for measurement of pH and Eh. Approximately every eight hours, the soil:water suspensions were analyzed for ferrous iron extracted with pH 2.8,  $\underline{N}$  NaOAc. The distilled water in the dialyzer tube was replaced at each four hour sampling and analyzed for P. The four hour sampling schedule was used because it was sufficient time to gain a measurable amount of P in the distilled water P "sink". After sampling, the compartments were purged with oxygen or nitrogen to maintain the desired conditions. A total of twelve water samples were withdrawn from the dialyzer tube and analyzed for P to obtain a measure of the kinetic factor under oxidized and reduced conditions.

#### Results and Discussion

The kinetic factor values shown in Table 3 were derived by multiplying the average P concentration for twelve water samples, times seventy-five (the volume of each water sample). Thus, the kinetic factor values represent the average  $\mu\text{g}$  P released from 100 g of soil to the water in the dialyzer tube during a four hour period.

Table 3. Effect of pH and oxidation state on the kinetic factor of ten soils

Soil No.	Oxidized Suspension			Reduced Suspension			Oxidized Suspension- pH Adjusted***		
	pH	P Conc. * (ppm)	Kinetic Factor** (ug P)	pH	P Conc. * (ppm)	Kinetic Factor** (ug P)	pH	P Conc. * (ppm)	Kinetic Factor** (ug P)
I-1	7.9	0.011	0.83	6.5	0.003	0.20	6.5	0.003	0.23
I-3	7.3	0.094	7.05	5.7	1.346	100.90	5.7	1.287	96.53
I-4	7.1	0.036	2.70	5.8	0.034	2.55	5.8	0.034	2.55
I-5	6.1	0.002	0.15	5.7	0.002	0.15	5.9	0.002	0.15
I-6	8.1	0.002	0.15	6.9	0.002	0.15	6.9	0.002	0.15
I-7	6.3	0.002	0.15	5.6	0.003	0.23	5.6	0.003	0.23
Pe-1	7.6	0.027	2.03	6.8	0.020	1.50	6.8	0.019	1.42
La-1	5.8	0.002	0.15	6.4	0.008	0.60	6.4	0.004	0.30
La-2	7.1	0.112	8.40	5.9	0.204	15.30	5.9	0.193	14.47
NC-2	6.0	0.002	0.15	5.9	0.002	0.15	5.9	0.002	0.15

\* P concentration in P "sink" after four hours. Average of twelve samples.

\*\* Quantity of P released from 100 g soil to P "sink" during four hour period.

\*\*\* pH adjusted with dilute acid or base to the pH of the reduced suspension.

The state of soil oxidation had no measurable effect on the kinetic factor of five of the ten soils (I-4, I-5, I-6, I-7, and NC-2). The I-5, I-6, and I-7 soils contain very little labile P, so this could explain why the oxidation state had no measurable effect on the kinetic factor. However, the I-5 and I-7 soils are typical of the Indian rice soils that show inconsistent or no response to P fertilizer. Reason for the lack of effect of oxidation state on the kinetic factor of the I-4 and I-6 soils is less evident because they contain considerable amounts of extractable P. The NC-2 soil contains twelve ppm P extractable with dilute acid ( $0.05 \text{ N HCl} + 0.025 \text{ N H}_2\text{SO}_4$ ) and I-4 released approximately twelve and one-half ppm P to an anion resin (Figure 1). However, their kinetic factors were not significantly affected by oxidation state.

The I-1 and Pe-1 soils exhibited significantly higher kinetic factors under oxidized conditions. This appears to be a result of an effect of pH rather than an effect of oxidation state because adjusting the pH of the oxidized sample to that of the reduced sample had the same effect as reduction had on the kinetic factor. For example, the pH in La-2 and I-3 samples decreased over one pH unit, from values between 7.5 and 8.0 to between 6 and 7 upon reduction. When the pH of these two soils was adjusted in separate oxidized samples to that of the reduced samples, the kinetic factor of these pH-adjusted, oxidized samples approximated those of the reduced soils.

La-1, La-2, and I-3 soils had higher kinetic factors under reduced conditions. For the La-2 and I-3 soils, the increased kinetic factor

under reduced conditions was the result of a pH change rather than the result of a change in oxidation state per se because adjusting the pH of the oxidized soil to that of the reduced soil had the same influence on the kinetic factor as reduction. However, soil La-1 exhibited higher P release rates under reduced conditions and this presumably was a result of the reduced conditions because adjusting the pH of the oxidized soil to that of the reduced soil did not increase the kinetic factor. Regardless of the mechanism responsible for the slightly greater kinetic factor in the reduced La-1 soil, the increased kinetic factor could help increase P availability in reduced La-1 soils.

It has been observed by a number of researchers (Ponnamperuma, 1955; Ponnamperuma and Castro, 1964; Patrick and Mikkelsen, 1971) that the pH of a soil tends to approach neutrality during anaerobioses. However, the pH values of the reduced La-2, I-3, I-4, I-5, I-7, and NC-2 soils were considerably lower than neutral in this experiment. The lower than normal pH was attributed to the accumulation of CO<sub>2</sub> within the cylinder containing sucrose as a readily available energy source. The potential of CO<sub>2</sub> for lowering the pH of alkaline soils has been well established by Bradfield (1941) and Whitney and Gardner (1943).

It is speculated that the reason CO<sub>2</sub> accumulation did not lower the pH of the La-1 soil was because the hydroxyl ions, released during the reduction of hydroxy-oxides of iron and manganese, tended to increase the pH more than CO<sub>2</sub> tended to decrease the pH. This speculation

agrees with Ponnampereuma and Castro's (1964)  $\text{Fe}(\text{OH})_3\text{-H}_2\text{O-CO}_2$  equilibrium theory as the dominant factor in controlling the pH of reduced soils. This also agrees with Patrick's (1964) explanation that the release of hydroxyl groups during reduction of iron compounds is responsible for the increase in pH occurring upon flooding an acid soil.

Even though the pH values observed in this laboratory experiment were somewhat unlike those expected under field conditions, the conclusions of the effect of reduction on the kinetic factor are valid for these soils when under field conditions. The reasoning behind this statement is that (1) the pH levels of most of these soils are such that they would not change appreciably during reduction under field conditions, and (2) pH rather than state of oxidation had the most pronounced effect on the kinetic factor in this experiment.

An additional point noted was the influence of soil pH on the amount of P released. This fact stresses the importance of the rhizosphere pH in influencing the P supply to plant roots. Of equal interest is the apparent constant rate of P release during the forty-eight hour period during which time the distilled water was replaced twelve times (once every four hours). For example, at pH 5.9, soil La-2 released approximately 15 ug P/100 g of soil every four hours over a forty-eight hour period. Fried and Shapiro (1952) also found that certain soils can supply P at a rather constant rate for at least fourteen successive one-hour water extractions.

In summary, the main point gained from this experiment is that only the kinetic factor of La-1 soil was slightly increased by reducing conditions. Reducing conditions did not increase the kinetic factor of nine soils; therefore, increased availability of P in these soils under flooding is due to an increase in a factor other than the kinetic factor.

#### Experiment 7: Effect of flooded conditions on the intensity factor

The P concentration of the soil solution is considered to be the intensity factor. It is recognized as one factor which sometimes limits the process by which P is supplied to plant roots from soil. This experiment was designed to measure the effect of reducing conditions on the intensity factor in an effort to determine if an increase in the intensity factor might be responsible for the increase in available P in flooded soils.

#### Materials and Methods

Data for this investigation were extracted from data generated in determining the E-value in Experiment 5. The details of methods are described there.

#### Results and Discussion

Figure 7 displays the effect of time and moisture treatment on the intensity factors of ten soils. The actual pH and Eh measurements are recorded in Table 2 of Experiment 5 and are discussed in Experiment 5.

The intensity factor was consistently greater under the waterlogged treatment for the three acid soils -- I-7, NC-2, and La-1. For the

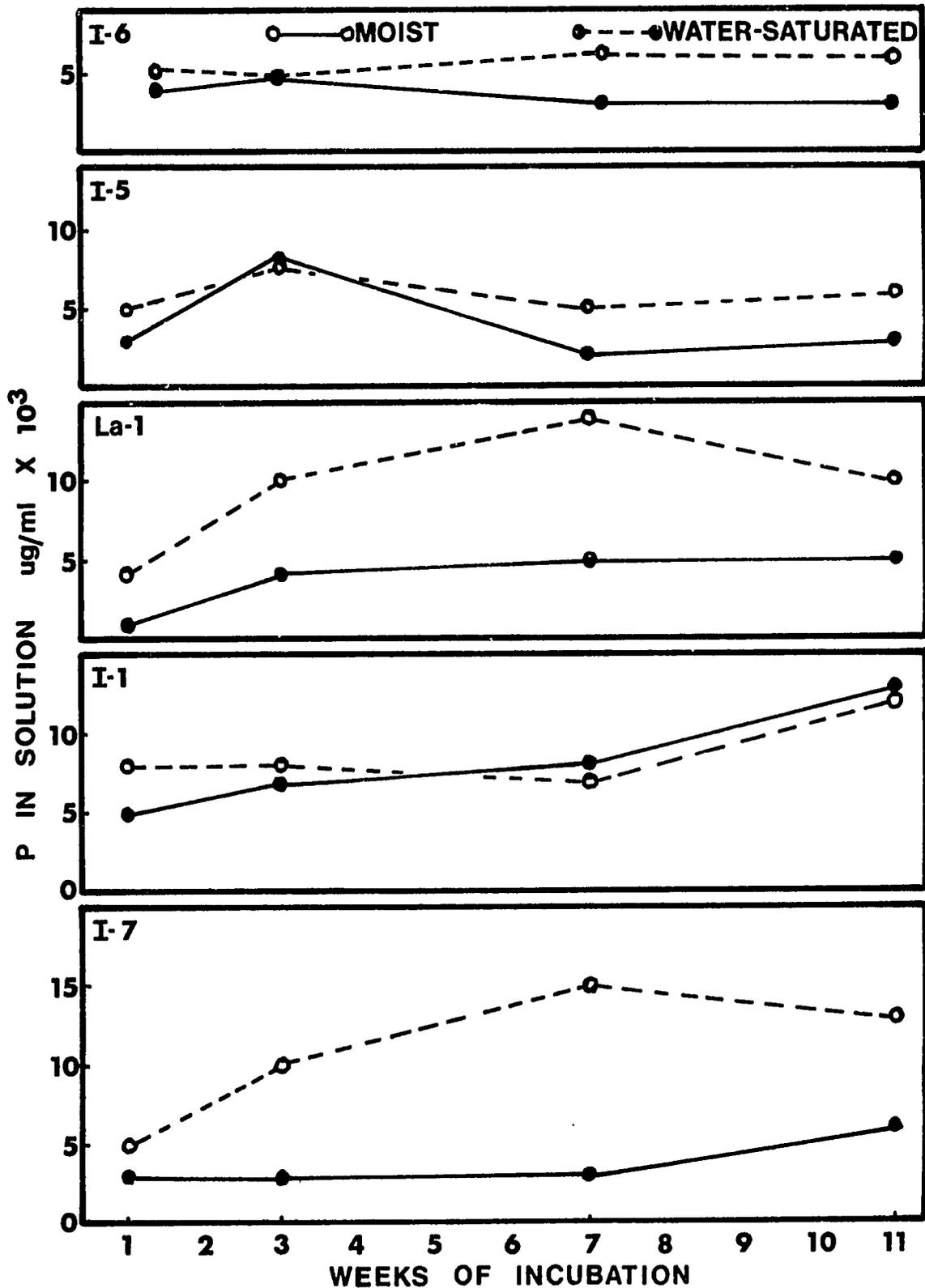


Figure 7. Comparison of soil solution P (intensity factor) in soils under moist (aerobic) and water-saturated (anaerobic) conditions. (Continued next page)

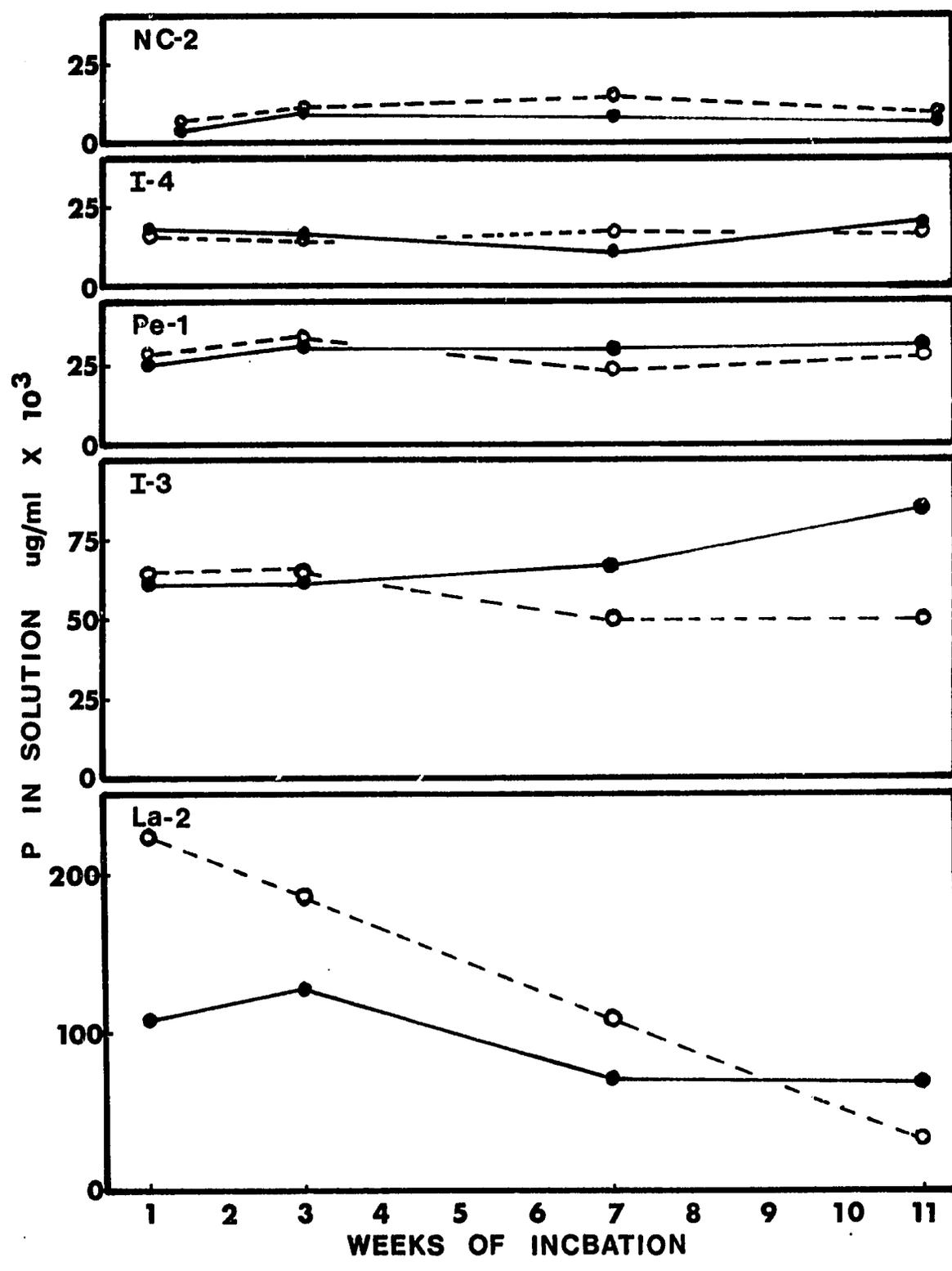


Figure 7. (Continued)

seven neutral to alkaline soils, the moisture treatment had little effect on the intensity factor or its effect varied with time after inducing the moisture treatment. Thus, it appears that waterlogging increases the intensity factor of acid soils; whereas, the intensity factor of alkaline soils is less influenced by waterlogging. This is what might be expected because reduction has little influence on calcium phosphates. Mahapatra and Patrick (1968) found that calcium phosphates were relatively unchanged by waterlogging and Broeshart, et al. (1965) suggested that the reduction of iron would not appreciably increase the solubility of P in a system where calcium is dominating as in an alkaline soil. Presumably any P released during reduction of ferric phosphate reacts with calcium compounds. However, the dominant P form in acid soils is likely iron and aluminum phosphates. The iron of iron phosphates may undergo reduction during soil anaerobioses, thereby releasing P (Ponnamperuma, 1955). Thus, the intensity factor could conceivably increase to some extent upon reduction of acid soils as shown in the results presented here. However, Tanaka, et al. (1969), in studying the P concentration in the soil solution of submerged soils, noted that any P released during anaerobioses of acid soils is likely combined with the reactive soil aluminum. They concluded that any increase in P concentration of acid soils is mainly a result of the increase in pH that occurs upon anaerobioses of acid soils. The increase in pH was observed in the reduced soils of this study. As Tanaka, et al. (1969)

further pointed out, the increase in pH results in an increase in the solubility of aluminum and iron phosphates.

Ponnamperuma (1965) provided data that illustrate that the intensity factor, or soil solution P, does not always increase upon flooding. He found that two of four acid soils did not have greater intensity factors after waterlogging. In the two soils in which the intensity factor did increase, the increase was followed by a gradual decrease. The decrease in the intensity factor began twenty days after waterlogging. He attributed the decrease to re-adsorption of P on clay or aluminum hydroxide. Thus, in light of Ponnamperuma's (1965) data, it is best not to generalize that the intensity factor of acid soils increases upon flooding, even though slight increases were consistently observed for the acid soils of this study.

Another point is that Hossner, et al. (1973) found 0.1 ppm P to be a near critical level for rice growth in pots containing Texas soils. However, the solution P concentrations (intensity factors) for the Indian soils of this study averaged nearly 0.01 ppm P and did not limit rice yields in field experiments conducted by the author in India. These apparently conflicting intensity factors illustrate that factors other than intensity influence P supply from soil to roots. Nambiar, et al. (1973) also observed a difference in the critical level of extractable P for rice grown under greenhouse and field conditions.

In summarizing the data from this experiment, it is evident that flooding of acid soils may increase their intensity factor slightly and

thereby increase P availability somewhat, possibly due to the increase in pH and its influence on solubility of iron and aluminum phosphates. However, reducing conditions had little effect on the intensity factor of alkaline soils of this study. These results agree with those of Mahapatra and Patrick (1969) and Broeshart, et al. (1965) who found that soil reduction did not have much influence on P solubility of a calcium system relative to an iron dominated system. Therefore, increased P availability upon flooding alkaline soils is not likely a result of an increase in the intensity factor.

#### Experiment 8: Effect of moisture on the diffusivity factor

Other researchers (Olsen, et al., 1961; Watanabe, et al., 1960; Mahtab, et al., 1971) have demonstrated that P diffusion rates in soils increase with moisture and have measured the rate of increased P diffusion with increasing moisture content below one-third bar moisture tension. However, no P diffusivity values could be found for soils with moisture contents from one-third bar to water-saturation. It is this latter moisture range which is important in rice culture. Therefore,  $^{32}\text{P}$  self-diffusion coefficients were determined at various soil moistures from near fifteen bars to water-saturation to measure the effect of water-saturation on the diffusivity factor.

#### Materials and Methods

Duplicate fifty gram subsamples of soil were saturated with water and then two drops of toluene were added to inhibit microbial growth.

Ten  $\mu\text{c}$  of  $^{32}\text{P}$  (as  $\text{H}_3^{32}\text{PO}_4$ ) were added to one subsample, and both subsamples were stirred every four to eight hours during a seven day equilibration period. Following the equilibration period, moisture was permitted to evaporate from the soils as a fan blew over the soil which was stirred vigorously at least once per hour. Moisture contents were monitored by weighing and the drying process was stopped at precise moisture values at which P diffusion rates were determined.

The diffusion cell used in determining  $^{32}\text{P}$  self-diffusion coefficients consisted of two plexiglass half-cells. Each half-cell constituted a short cylinder ( $h = 0.5 \text{ cm}$ ,  $r = 2 \text{ cm}$ ) which was capped at one end. Soil of known moisture content was placed firmly into each half-cell. Soil containing  $^{32}\text{P}$  was placed in one half-cell and non-labeled soil in the other half-cell. Thus, each pair of half-cells contained the same soil at an identical moisture, but the soil in one half-cell was tagged with  $^{32}\text{P}$ . The open ends of each pair of half-cells were joined together so that the labeled and non-labeled soils were in contact forming a diffusion cell. A nylon mesh fabric was placed between the labeled and non-labeled soils just prior to joining them. The mesh fabric helped achieve a clean separation after the seven day diffusion period. During the diffusion period, the diffusion cell was sealed with tape, bound together with a "C" clamp, and incubated in a humid atmosphere at a room temperature of approximately  $23^\circ \text{C}$ .

After the diffusion period, the half-cells were separated, the soils removed, and digested with 100 ml of N  $\text{H}_2\text{SO}_4$  for one hour in a  $90^\circ \text{C}$

water bath. The digestate was brought to a 100 ml volume by adding water to regain the original weight and aliquots were taken for  $^{32}\text{P}$  assay by liquid scintillation. Self-diffusion coefficients (D) were calculated using the following equation:

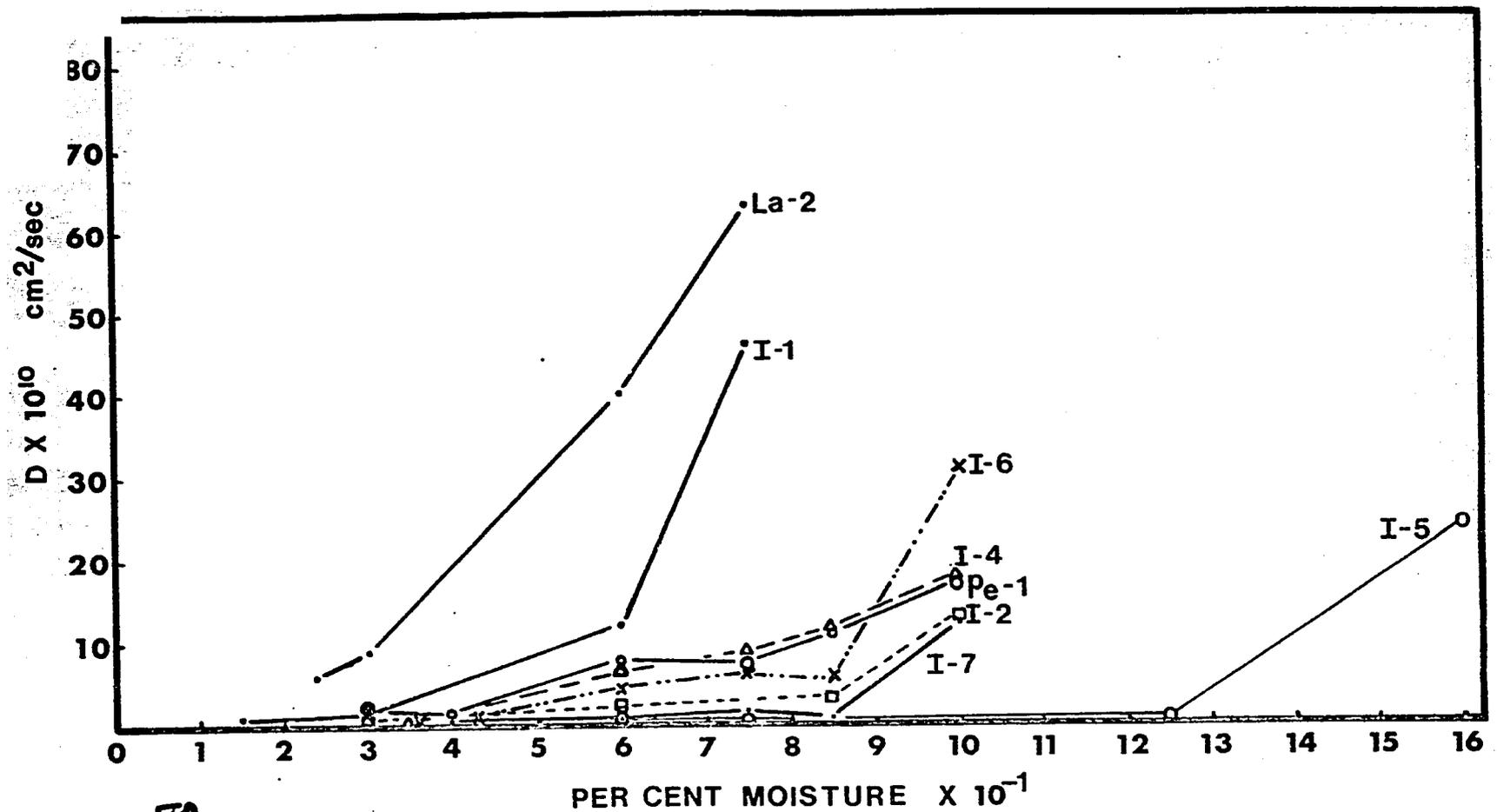
$$\frac{Q}{Q_{\infty}} = \frac{2}{L} \left[ \frac{DT}{\pi} \right]^{\frac{1}{2}}$$

in which Q is the quantity of  $^{32}\text{P}$  diffusing into the non-labeled soil after time -- T,  $Q_{\infty}$  is one-half the original  $^{32}\text{P}$  in the labeled soil, and L is the thickness of each soil through which diffusion can occur. This equation or a modification of it has been employed by Olsen, et al. (1965), Phillips (1969), and Mahtab, et al. (1971).

#### Results and Discussion

The  $^{32}\text{P}$  self-diffusion coefficients (D-values) plotted in Figure 8, approximate those which Mahtab, et al. (1971) reported for soil moistures at tensions one-third bar or higher, and they pointed out that their D-values paralleled those obtained by Lewis and Quirk (1967), Olsen, et al. (1965), and Phillips, et al. (1968).

A noteworthy point is that water-saturation, represented by the highest soil moisture level for each soil in Figure 8, resulted in at least a ten-fold increase in the diffusivity factor relative to the lowest soil moisture levels. Since the effects of waterlogging on increasing the capacity, kinetic, and intensity factors were slight and/or infrequent, while the increases in the diffusivity factor were pronounced



50  
 Figure 3. Effect of moisture on the diffusivity factor (D-values or <sup>32</sup>P self-diffusion coefficients). The final point on each curve represents D-values at water-saturation. I = Indian Vertisid, Pe = Peruvia Mollusid, La = Louisiana Mollusid.

and occurred for every soil, it is suggested that increases in the diffusivity factor could explain the increase in P availability that occurs upon flooding.

Since these soils contained toluene (two drops per fifty grams of soil) to inhibit microbial growth, one would not expect the water-saturated soil to be reduced. If the water-saturated soils were reduced, as they are under field conditions, then water-saturation could have resulted in a greater than ten-fold increase in the diffusivity factor because of a decrease in the soil's P fixation capacity as iron became reduced. Increases in P diffusion resulting from a decrease in P fixation capacity was considered in a discussion of the relative importance of P diffusion and reduction on anion resin adsorbable P (Experiment 4). It was noted at that time that Place, et al. (1968) had shown P fixation to increase with iron oxide content of soils. From this point of view, it seems logical that water-saturation coupled with a reduced soil environment associated with field conditions would enhance the diffusivity factor even more than the ten-fold increase that was recorded in the absence of a reducing environment.

A higher P self-diffusion coefficient for the La-2 soil relative to the other soils in Figure 8, is indicative of the relatively high water-soluble P concentration (approximately 0.1 ug P/ml) for soil La-2 compared to an average of approximately 0.01 ug P/ml for the other soils. Phillips, et al. (1968) and Mahtab, et al. (1971) have shown that increased concentration of soil solution P enhances D-values.

One observation evident here, but not in earlier reports, is that for very fine-textured soils of low P concentration and high P fixation capacity, increased soil moisture has little effect on D-values until the soils are completely water-saturated. Soils I-2, I-5, and I-6 typify such soils. The resistance of I-5 to respond to increased soil moisture with increased D-values, is attributed to its very high smectite clay content and water holding capacity.

It is recognized that the bulk density in the diffusion cells decreased as soil moisture increased in the soils of this study due to the dilution effect of water and the swelling of the smectite clays. Therefore, part of the increase in P diffusion in water-saturated soils could be due to reduction in soil bulk density. But the fact that water-saturation of soils increases P diffusion is still valid since this decrease in bulk density exists under field conditions for lowland rice.

An additional comment is that stirring the soil during the seven day equilibration period and during the drying process increased the water holding capacity of the soil, presumably by exposing additional silicate surfaces not exposed in the aggregated state existing prior to stirring. This is evidenced in that soil I-5, in the aggregated state, had a one-third bar moisture of 57 per cent, but after continued stirring, the soil was so "dry" that it could not be pressed into the diffusion half-cell at a moisture content of less than 60 per cent. This observation follows the findings of Taylor (1972) who reported that

mechanical energy may disrupt existing soil structure and increase the water retention at a specific potential.

Recalling that Watanabe, et al. (1960) and Mahtab, et al. (1972) showed that P availability to plants increased with moisture at moisture contents above one-third bar tensions as a result of an increase in the diffusivity factor and noting that pronounced increases in D-values were recorded at soil moistures below one-third bar suggests the following conclusion: The increase in the diffusivity factor upon water-saturation could largely explain the increase in P availability that results from flooding a soil. The conclusion is supported by the following three points:

(1) The effect of flooding on the capacity, kinetic, and intensity factors in the P supply from soil to root were slight and inconsistent, while the effect of flooding on the diffusivity factor was at least a ten-fold increase and consistent with each soil.

(2) P diffusion is a major mechanism by which P is transported to root surfaces (Olsen, et al., 1962; Barber, et al., 1963) and has been shown to account for 95 per cent of the P adsorbed by lowland rice plants (Folsom and Hossner, 1973).

(3) Watanabe, et al. (1960) and Mahtab, et al. (1972) have demonstrated that P availability increases with moisture in the moisture range above one-third bar tensions as a result of increases in the diffusivity factor and Figure 8 shows that the diffusivity factor is greatest in water-saturated soils.

Thus, it follows that the increased P availability upon flooding a soil is largely a result of an enhancement of P diffusion. It was felt that if this conclusion were true, one should be able to demonstrate it experimentally using plant growth and P uptake as indications of P availability. Such an experiment was conducted and is described in the following section.

Experiment 9: Effect of soil moisture on P availability as measured by growth of rice plants free of water-stress

Since increasing soil moisture increases the diffusivity factor, a major limiting factor in the supply of P from soil to root, it follows that increasing soil moisture should increase P availability to lowland rice. This assumption is valid if a significant proportion of the P required by rice plants arrives at the plant root by diffusion and there is considerable evidence that diffusion is the major mechanism by which P is transported to roots. Olsen, et al. (1972) and Barber, et al. (1963), studying unsaturated soils, and more recently Folsom and Hossner (1973), working with water-saturated rice soils, support the contention that P diffusion is the dominant mechanism by which P arrives at root surfaces. Hence, it seems probable that plant available soil P is likely increased by increasing soil moisture. Difficulties are encountered in testing this hypothesis because a change in soil moisture alters (1) the diffusion of plant nutrients other than P, (2) water-stress of plants, and (3) the oxidation state of soils (particularly

in water-saturated soil). Therefore, experimentally testing the hypothesis, that P availability increases with soil moisture, was precluded by the development of experimental techniques which separated the various effects of moisture.

#### Materials and Methods

By modifying the split root technique of Mengel and Von Braunschweig (1972) to meet our requirements, the water-stress problem and the effect of moisture on the diffusion of nutrients other than P were eliminated. In this technique one part of the root system was bathed in a minus P nutrient solution (Yoshida, et al., 1970, pg. 54) and the other was in contact with soil. The soil provided the only source of P and soil moisture was maintained at specific values to measure the influence of soil moisture on P availability.

In an attempt to eliminate the effect of reduction on P availability (i. e., release of P during reduction of oxidized P compounds), the I-6 soil was used as a test soil. It was felt that the amount of reductant soluble P in the I-6 soil would be insignificant because of its calcareous nature and very low labile P content. Soil NC-1 was also selected as a test soil because of its low P content.

The soil container (Figure 9) was initially three-fourths filled with soil which was moistened by tension-free water in a porous porcelain bulb. The porcelain bulb, constructed by epoxying two porcelain suction cups together, had such fine pores that air was not pulled through the moist porcelain material at tensions used in this

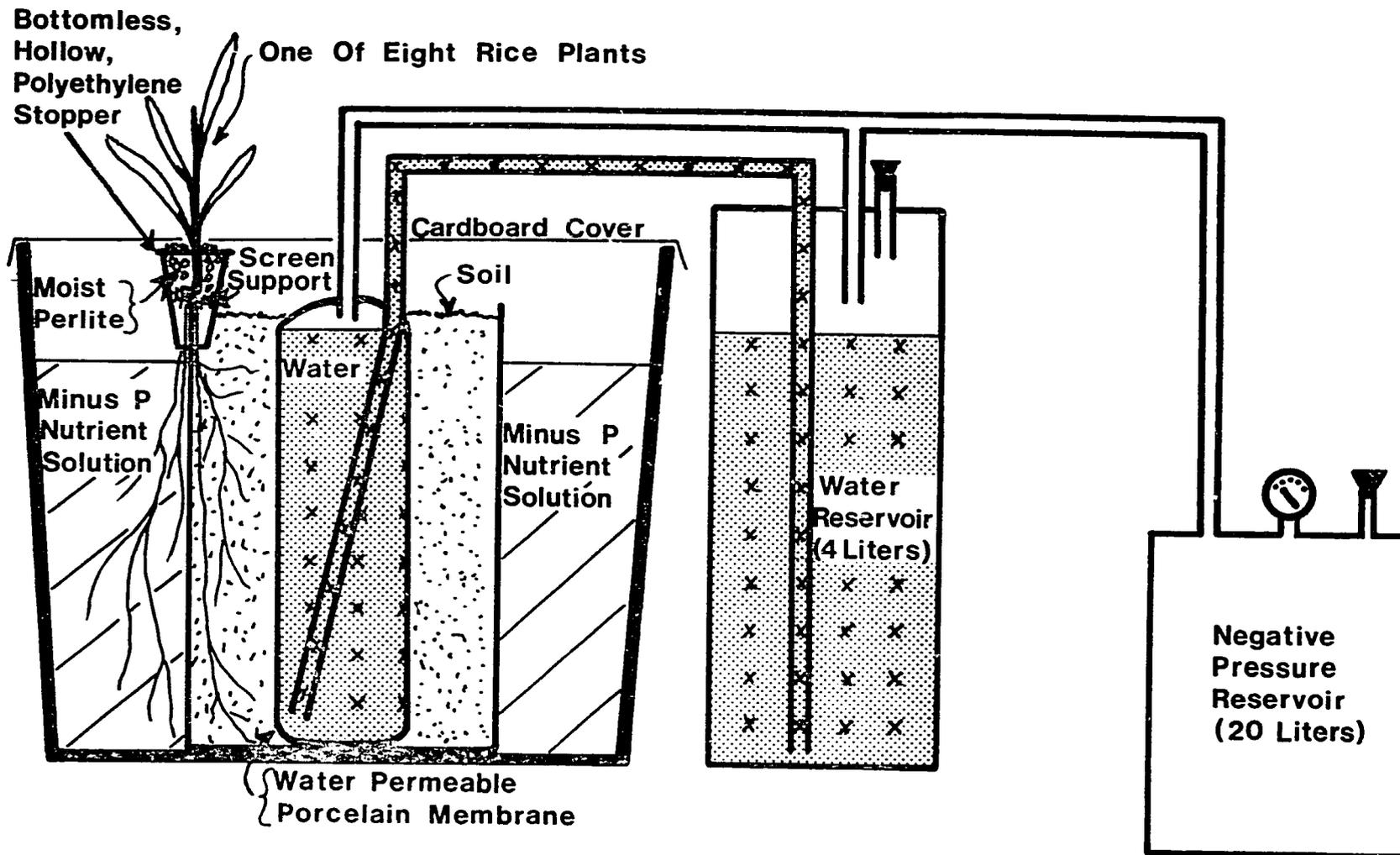


Figure 9. Diagram of apparatus used to control moisture in soil and powdered cellulose growth medium

study. After the soil was moistened, moisture tension treatments of zero, five, fifteen, twenty-five, or thirty-five centibars (cb) were placed on the water in a bulb by applying suction to the vacuum reservoirs. Each vacuum reservoir served three porcelain bulbs, which were the three replicates of each moisture tension treatment. Vacuum gauges were used to monitor the tension. Moisture tensions were checked at least twice a day. The five moisture tensions remained relatively constant throughout the four week plant growth period, creating a range in soil moisture from water-saturated to near air dry from which plant roots could adsorb P. Under the thirty-five cb tension the soil was much drier than the implied near one-third bar or field capacity moisture. Corresponding more closely to field capacity was the five cb treatment. After the soil had reached equilibrium at the applied tension, eight two-week old rice plants of Saturn variety, which had been grown in the nutrient solution described by Yoshida, but with only one-fourth of the P concentration, were placed on the rim of the soil container. Equal portions of the root system extended into the soil container and into the nutrient solution container. The soil container was then filled with soil, making a total volume of approximately 650 ml. After moistening the soil, minus P nutrient solution was added to the outside container which contained black, floating, polypropylene beads to restrict light entry into the solution. Both the inner and the outer containers were covered to help prevent evaporation, but still allow weekly replacement of nutrient solution.

Rice plants on the I-6 soil, fertilized with 150, 80, and 50 Kg/ha of N, P [as  $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ], and K, respectively, were grown in a greenhouse, from June 1 through June 28, with day-night greenhouse temperatures of 24 and 32° C. At similar day-night greenhouse temperatures during July 3 through July 31, rice plants were grown on the NC-1 soil fertilized with 100, 30, and 50 Kg/ha of N, P, and K, respectively. After four weeks of growth, tiller counts were made and shoots harvested and analyzed for P. Samples of the shoots taken at transplanting were also analyzed for P in order to compute P uptake.

The technique and apparatus described above, allowed rice plants to obtain their water supply and nutrient requirements other than P from a nutrient solution. The rate of P fertilization of the soil was selected so that P was the growth limiting factor and it was supplied by a soil maintained at various moistures. Therefore, if moisture does influence soil P availability, the influence should be reflected in terms of plant parameters.

#### Results and Discussion

There was a difference noted in the rice growth on the two soils (Table 4). This may have been a result of slight environmental differences since the growth periods were at different times. It may also reflect a plant growth limitation inherent in the NC-1 soil which had the smaller amount of growth. However, the soil was fertilized with limited amounts of P and ample amounts of N and K, and limed to pH 6.5. All nutrients other than P were supplied by the nutrient

Table 4. Effect of soil moisture on P availability in two soils as measured by shoot growth and P uptake of rice plants free of water-stress

Moisture Treatments (centibars)	Dry Wt. <sup>2</sup> Tops (grams)	Shoot P Accumulation (ug P/pot)	P in Shoots (%)	Extractable Fe <sup>++</sup> (ug/g)	Soil Moisture <sup>3</sup> (%)
<u>Soil I-6</u>					
0 <sup>1</sup>	4.73a <sup>4</sup>	1331	.08	50.0	63.0
5	4.35ab	1676	.09	0	43.0
15	3.78bc	410	.07	0	28.0
25	3.60bc	236	.07	0	25.0
35	3.43c	-30	.07	0	26.0
<u>Soil NC-1</u>					
0 <sup>1</sup>	2.60a	1898	.08	2325.0	23.6
2	1.29b	463	.05	1.2	11.6
15	1.32b	578	.05	1.1	6.1

1 Water-saturated treatment

2 Average of three replications (eight plants/replication)

3 Moisture content at harvest

4 Values followed by the same letter are not significantly different at the 5 per cent level of probability as tested by Duncan's multiple range test

solution which bathed a portion of the plant roots, thus the lack of growth in soil NC-1 relative to soil I-6 may have been due to a nutrient imbalance.

Theoretically, the thirty-five cb moisture tension should have created a soil moisture value near one-third bar. However, in preliminary studies and in this study, it was found that a five cb tension on the porcelain bulb came closer to maintaining a one-third bar soil moisture. For example, 43 and 11 per cent soil moisture for the five cb tension, approximated one-third bar moisture tensions for the I-6 and NC-1 soils, respectively. The reason why the fifteen, twenty-five, and thirty-five cb treatments produced nearly the same soil moisture values in the I-6 soil is not readily apparent, but the 28, 25, and 26 per cent soil moistures apparently represent the true soil moisture at the given tensions because there were no significant differences in growth or P uptake within these soil moisture values. Where increases in soil moisture were evident (26 to 43 per cent in soil I-6 and 6 to 23.6 per cent in soil NC-1), increases in shoot growth and P uptake were evident too. It was assumed that P accumulation in shoots was directly related to P uptake. Thus, in general, these data indicate that increases in soil moisture increase P availability as measured by P uptake and shoot growth. These results are supported by the studies of Mederski and Wilson (1960), Watanabe, et al. (1960), Olsen, et al. (1962), Wesley (1965), Mahtab, et al. (1972), and Sanchez and Briones (1973). Most of these previous studies were conducted with aerable crops and mois-

ture tensions greater than one-third bar. They attributed the observed increase in P availability, as soil moisture increased, to the increase in P diffusion as soil moisture increased.

The results of this experiment also agree with the results of a group of scientists studying moist and saturated soils. However, the interpretation of the results presented here, is in contrast with their interpretations. They used A-value techniques (Shapiro, 1958a; Valencia, 1962; DeDatta, et al., 1966) and plant growth (Davide, 1960), to show that the availability of P to rice increased when moist soils became water-saturated. These scientists, working with flooded soils, attributed the increase in P availability upon flooding to the release of P from oxidized iron phosphates as the soil was reduced.

Assuming that P is released during reduction of ferric phosphate, the presence of ferrous iron in the water-saturated treatments of soil I-6 and NC-1 (Figure 9) prevents the conclusion that the increase in P availability under the water-saturated condition is due totally to diffusion. Similarly, the increase in growth upon water-saturation of soil I-6 cannot be totally attributed to reductant soluble phosphorus (R. S. P.), since it was evident from growth in soil I-6 that soil moisture increased P availability. For instance, as soil moisture increased from 26 to 43 per cent, shoot growth and P uptake, the two indicators of P availability, increased. This suggests that the increase in P availability upon flooding could be attributed to an increase in P diffusion rather than a result of the release of P during the reduction of iron phosphates.

However, the possibility of R. S. P. becoming a source of P in reduced soil cannot be ruled out even though I-6 and NC-1 soils were selected because of their lack of R. S. P. Also, nitrates were applied to the soil as a source of N to retard reduction.

Murayama (1965) reviewed the mineral nutrition characteristics of various organs of the rice plant and revealed that the youngest leaves contained about 0.7 per cent P and the oldest contained 0.08 per cent or less P. Likewise, he noted that P concentration in plant tissue varied with plant growth stage; thus, he surfaced some of the complications of trying to relate the percentage of P in shoots to P deficiency. P deficient rice straw in Japan and in the Philippines has been reported to contain 0.08 and 0.04 per cent P, respectively (IRRI Annual Report, 1965, pp 46-47). In contrast, two varieties of rice plants growing in adequate, but not excessive, P nutrient solutions (as indicated by no reduction in panicle weight relative to the control), contained 0.17 and 0.10 per cent P in straw at harvest for the Tainan 3 and Peta varieties, respectively (IRRI Annual Report, 1964, pg 78). In light of these results, the P percentage in the shoots of this study (Table 4) indicates that soil P concentration at root surfaces was limiting the P supply as anticipated. Thus, P transport to root by diffusion should have been a limiting factor and moisture should have and did influence P availability.

Not being satisfied with these results, an additional experiment was conducted in which the growth medium contained no R. S. P. The

experiment, described in Experiment 11, was designed to separate the influence of moisture from the influence of reduction on P availability in an attempt to determine if the increased P availability that occurs upon flooding could be attributed to increased P diffusion.

Experiment 10: Effect of moisture and solution P concentration on  
P diffusion in powdered cellulose

The purpose of this experiment was two-fold: To determine if P diffusion increases with moisture of the cellulose growth medium and to observe the effect of solution P concentration on P diffusion in this medium.

Materials and Methods

Powdered cellulose samples containing 1 per cent tricalcium phosphate or an equivalent amount of P as monocalcium plus dicalcium phosphate were dried at 70° C, then 1.2 g of P treated cellulose were placed in each of two plexiglass half-cells described previously in Experiment 8. The cellulose in each half-cell was saturated with water and then the cellulose in one of the half-cells was labeled with five  $\mu\text{C}$  of  $^{32}\text{P}$ . The water-saturated cellulose was patted until smooth and free of air pockets. After a three day equilibration period, which allowed some water evaporation, the cellulose could be removed from the half-cell as a firm moist disk four cm in diameter and 0.35 cm thick. As the cellulose disks were turned from one side to the other in an air current, they lost moisture. When the moisture content of

the cellulose disks reached either 400, 200, 100, or 50 per cent moisture, they were placed in a humid environment. A non-labeled disk was then placed congruently on a labeled disk, and the two disks were sandwiched between the flat sides of the plexiglass half-cells. The plexiglass half-cells were wrapped with masking tape to help prevent water evaporation, then placed in a humid environment for a seven day diffusion period. The cellulose disks were then separated, air dried, placed in fifty ml of one normal nitric acid and mixed. After allowing the cellulose to settle to the bottom, the acid solutions were assayed for  $^{32}\text{P}$  by liquid scintillation. The equation described in Experiment 8 was used to calculate D-values for a measure of P diffusion in powdered cellulose. Duplicate diffusion determinations were made for each moisture level for both P sources.

#### Results and Discussion

It is evident from the results given in Table 5, that P diffusion in powdered cellulose increases with moisture and P concentration, and is greatest when the cellulose is saturated with moisture. The solution P concentrations in the water-saturated treatment for the tricalcium phosphate and for the monocalcium plus dicalcium phosphate were estimated to be 0.7 and 370 ug P/ml solution, respectively. D-values obtained in the tricalcium phosphate treated cellulose are comparable to those for soils given by Mahtab, et al. (1971). They noted that their D-values approximated those of Olsen, et al. (1965) and Phillips, et al. (1968). D-values observed in monocalcium plus dicalcium

phosphate treated cellulose were considerably higher than those found by Mahtab, et al. (1971), but are not as high as the D-values reported by Lewis and Quirk (1967) who used high P concentrations (50 to 2,000 ppm) not usually found in soils.

Table 5. Effect of moisture and high (monocalcium plus dicalcium phosphate) and low (tricalcium phosphate) solution P concentration on P diffusion in cellulose

Moisture in cellulose (%)	D-values X $10^{10}$ cm <sup>2</sup> /sec	
	Tricalcium phosphate	Monocalcium plus dicalcium phosphate
50	1.89	610
	1.77	760
100	4.36	642
	5.51	729
200	35.8	1240
	35.1	1330
400	197.0	1460
	374.0	1360

Although diffusion was greater when the solution P concentration was higher, the actual effect of moisture on P diffusion was greatest when the solution P concentration was lowest. This conclusion is based on the observation that D-values for the tricalcium phosphate and the monocalcium plus dicalcium phosphate treatments increased from an average of  $685 \times 10^{-10}$  and  $1.8 \times 10^{-10}$  cm<sup>2</sup>/sec to  $1410 \times 10^{-10}$  and  $285 \times 10^{-10}$  cm<sup>2</sup>/sec, respectively as moisture increased. This

represents an increase by a factor of 2.05 when P concentration was relatively high (monocalcium plus dicalcium phosphate treatment) and an increase by a factor of 158 when the P concentration was lower (tricalcium phosphate treatment) as the moisture increased from 50 to 400 per cent. These data will be discussed in the next section which relates growth of rice plants to increases in P availability with increasing moisture of the powdered cellulose growth medium.

The point of emphasis here is that P diffusion in powdered cellulose increases with increasing moisture and P concentration, as does P diffusion in soils. Likewise, the D-values in cellulose are comparable to those observed in soils.

**Experiment 11: Effect of moisture on the availability of P in a growth medium free of reductant soluble P**

In an attempt to determine if flooding per se increases the availability of P, it was necessary to separate the effects of reduction as a result of water-saturation on P availability. To measure the effects of water-saturation per se on soil P availability is most difficult because it is practically impossible to water-saturate an unstirred soil without inducing anaerobioses. Therefore, an inert, artificial growth medium was used in place of soil. Because of its large surface area, low iron and manganese content, high water holding capacity, and relative inertness, powdered cellulose was employed as an artificial growth medium.

## Materials and Methods

The split root technique described in Experiment 9 and shown in Figure 9 was used in this experiment, except powdered cellulose replaced the soil as a growth medium. For the first greenhouse experiment, reagent grade  $\text{Ca}_3(\text{PO}_4)_2$  was mixed with powdered cellulose to obtain an artificial growth medium containing 1 per cent  $\text{Ca}_3(\text{PO}_4)_2$ . This provided a growth medium with a relatively low solution P concentration (approximately 0.7 ug P/ml) so that moisture would significantly influence P diffusion and therefore P availability and plant growth. In the second experiment, the same amount of P was added to the cellulose, but one-half as monocalcium phosphate and one-half as dicalcium phosphate rather than the tricalcium form of P. This created a solution P concentration of approximately 370 ug P/ml for the water-saturated treatment. Thus the second experiment had a high solution P concentration so that even limited diffusion in the low moisture treatments should provide sufficient P so that P supply would not limit plant growth.

## Results and Discussion

The lower shoot weight of plants grown on the cellulose treated with monocalcium plus dicalcium phosphate (M+DCP) relative to the shoot weight of plants grown on the tricalcium phosphate (TCP) is attributed to the lower solar radiation and temperature during the growth period of the M+DCP plants (Table 6). The TCP experiment was conducted during October and the M+DCP during November and December.

Table 6. Effect of moisture and solution P concentration on P availability in P treated powdered cellulose as measured by shoot growth and P uptake of rice plants free of water-stress

P Source	Imposed Tension (cb) <sup>1</sup>	Shoot Weight (g)	Shoot P Accumulation (mg/pot)	Maximum Growth (%)	Moisture in Cellulose (%) <sup>4</sup>	P In Shoot (%)
Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub>	0 <sup>2</sup>	7.48a <sup>3</sup>	16.0a	100	365	0.23
	2	6.00b	6.1b	80	150	0.12
	5	4.44c	5.0b	59	135	0.14
	15	3.57c	2.4c	48	125	0.10
CaHPO <sub>4</sub> plus Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	0 <sup>2</sup>	4.77a	21.0a	100	331	0.42
	2	5.05a	17.3a	91	143	0.39
	5	4.76a	18.4a	89	143	0.42
	15	4.61a	13.0b	86	134	0.35

1 Centibars

2 Water-saturated treatment

3 Values followed by the same letter are not significantly different at the 5 per cent level of probability as tested by Duncan's multiple range test

4 Moisture content at harvest

Although little trouble was encountered in maintaining the tension in the porcelain bulbs at prescribed settings, at harvest, the cellulose (with the exception of the water-saturated treatment) was considerably drier than it was in preliminary evaluation of the moisture control apparatus. In the preliminary evaluation, cellulose moisture was determined after the cellulose had been under the desired tension for two days while the growth period was four weeks. This indicated a gradual drying of the cellulose during the growth period. Also since the roots were more concentrated near the porous porcelain bulb, a moisture gradient, decreasing away from the bulb, may have existed in the cellulose. However, the main purpose of the apparatus was to create a range in moisture from saturated to near dry and this was accomplished. The percentage of moisture in the cellulose growth medium was within the moisture range, 50 to 400 per cent, used in Experiment 10 where P diffusivity was measured. Since P diffusion was found to increase with moisture, P availability should have increased with moisture. This was observed in the TCP treated cellulose which had a solution P concentration of approximately 0.7 ug P/ml (Table 6). An increase in P availability with moisture is evidenced by the increase in shoot growth and P uptake by the plants. It was assumed here, as in Experiment 9, that P accumulation in shoots was directly related to P uptake. These data from the TCP experiment show that moisture had a significant effect on P uptake and shoot growth. The data support the hypothesis that the greatest effect

of water-saturation on P availability is through its enhancement of P diffusion, rather than a result of the release of soil P during reduction. Since the growth medium was devoid of reductant soluble F, reduction could have had no effect on P solubility. The 0.7 ug P/ml solution P concentration in the TCP treated cellulose was higher than expected, but the percentage of P in shoots (Figure 6) indicates that P was limiting growth in the two, five, and fifteen cb treatments.

It was observed that the roots in the water-saturated cellulose were of large diameter and unbranched relative to the more fibrous and branched roots in the non-water-saturated cellulose. This suggests that the greater P uptake from the water-saturated treatment occurred despite the apparent greater root surface for P absorption in the low moisture treatments.

There was no significant effect of moisture on shoot growth when M+DCP was the P source. There was a significant reduction in P uptake at the lowest moisture level, but P uptake at the lowest moisture level apparently did not limit shoot growth as evidenced by the percentage of P in the shoot and the shoot weight.

These M+DCP data are interpreted to indicate that all of the increased P availability with increased moisture in the TCP treated cellulose was not a result of a factor inherent in the apparatus. Neither was it a result of an increase in the root absorbing surface, nor a result of the reduction of ferric phosphate. It was a result of an increase in P diffusion to the root surfaces.

## Summary of Results and Discussion of Chapter V

The general objective of the research reported in this chapter was to assess the effect of water-saturation on the capacity, kinetic, intensity, and diffusivity factors in the P supply process from soil to plant roots. It was felt that observing the effect of flooding on these four factors would provide insight into the mechanisms responsible for the increased availability of P observed upon flooding a soil.

It was found that anaerobic conditions per se did not increase the kinetic factor in nine of the ten soils used in this study as measured by the release of P from a soil to distilled water which served as a P "sink". Therefore, increased P availability upon flooding of these soils is not due to an increase in the kinetic factor. However, the kinetic factor of the acid, La-1 soil did increase slightly on anaerobioses; hence anaerobic conditions, associated with flooded soils, could explain a slight increase in P availability on flooding this soil.

Water-saturation and thus reducing conditions increased the capacity factor, as measured by E-value, of the I-3 and La-2 soils, but had no definite effect on the capacity factor of the eight other soils. The increased capacity factor of the alkaline La-2 and I-3 soils was initially thought to be due to the lower pH (approximately one-half pH unit lower) associated with the flooded relative to the moist condition. These two soils are calcareous and apparently the isotopic exchangeability of their P compounds increases with a decrease in pH. However, alkaline soils I-1, I-6, and Pe-1 decreased in pH, but their E-value did not increase

as it did in soils I-3 and La-2. The reason for the increase in E-values in two alkaline soils and no change in E-values for the other five alkaline soils upon flooding remains unclear at present.

Data were obtained that suggest flooding may increase the intensity factor of an acid soil as was evidenced by an increase in the intensity factor of all three acid soils (I-7, NC-2, and La-1) upon flooding. However, flooding had essentially no measurable effect on the intensity factor of the seven alkaline soils of this study. Thus, increased P availability upon flooding of alkaline soils is not attributed to an increase in the intensity factor.

Laboratory investigations of  $^{32}\text{P}$  self-diffusion coefficients in soils, showed that water-saturation of a soil increased P diffusion coefficients at least ten-fold as compared to those observed in soils slightly below fifteen bar moistures. Hence, water-saturation caused large increases in the diffusivity factor of all soils studied.

Data from the initial experiments with ten soils reveal that flooding slightly increased the kinetic factor of only one acid soil (La-1), increased the intensity factor of three acid soils (La-1, NC-2, and I-7), and increased the capacity factor of only two alkaline soils (La-2 and I-3). Thus, the increases in the capacity, kinetic, and intensity factors upon flooding were slight and infrequent, while the increase in the diffusivity factor was pronounced and consistent for both acid and alkaline soils. These data provide evidence that the increase in P availability upon flooding is due primarily to an increase

in the diffusivity factor rather than any effect of reducing conditions associated with flooded soils. The following observations also support this diffusion hypothesis.

(1) Release of P during reduction of ferric phosphates (Aoki, 1941; Eriksson, 1952) may be a possible source of increased availability of P upon flooding. However, Broeshart, et al. (1965) contend that the reduction of iron would not have as great an influence on the solubility of P in a system where Ca is dominating; yet increased P availability is evident in flooded calcareous soils (Nambiar, et al., 1973).

(2) There is considerable evidence (Alberda, 1953; Mitsui, 1965; Yoshida, 1966; Uemura and Moriya, 1969; Hoshino, et al., 1970) that the rhizosphere of rice plants is oxidized. Assuming it is oxidized, any beneficial effect of reduction on P availability may be totally masked by the oxidized rhizosphere.

It was concluded from the above observations and experiments with the capacity, kinetic, intensity, and diffusivity factors, that the increased P availability upon flooding acid and alkaline soils is a result of the increase in the P diffusivity factor rather than any effect of reducing conditions induced by flooding. It was felt necessary to employ rice plants to verify this initial conclusion.

Experiments were conducted using split root techniques that allowed rice plants to obtain all needed water and nutrients other than P from a nutrient solution. The only source of P was a soil maintained at various moisture levels. From these experiments, evidence

was obtained to support the hypothesis that increased soil moisture increases P availability through enhancement of P diffusion. Due to the anaerobic conditions induced by water-saturation of the soil, all of the increase in P availability upon flooding could not be attributed to an increase in P diffusion since anaerobic conditions may have increased the availability of reductant soluble P. In a second plant growth study, reductant soluble P as a possible source of P in the water-saturated treatment was eliminated by growing rice plants in tricalcium phosphate treated cellulose maintained at various moisture tensions. P diffusion coefficients in the P treated cellulose approximated those found in soils. In the cellulose as in the soil, shoot growth and P uptake increased with moisture of the growth medium and maximum growth was obtained in the water-saturated treatment.

A third plant growth experiment was conducted using monocalcium plus dicalcium phosphate to provide a very high P solution concentration in the cellulose growth medium so that sufficient P was supplied to plants regardless of the restrictions placed on P diffusion by low moisture in the cellulose growth medium. Under this condition of higher solution P concentration, moisture had little influence on P availability. This indicated that the P availability increase that occurred upon water-saturation of the tricalcium phosphate treated cellulose was due to increased P diffusion rather than a factor inherent in the experimental design.

The data reported in this chapter are interpreted to indicate that much of the increased P availability in acid soils and most of the increased P availability in alkaline soils that occur upon flooding, can be attributed to an increase in the diffusivity factor.

## CHAPTER VI

## GENERAL SUMMARY AND CONCLUSIONS

The three approaches used in this study to evaluate the increased P availability that occurs upon flooding a soil were a study of the factors in the P supply from soil to root, plant growth, and anion resin experiments. An anion resin, in stationary contact with a water-saturated soil, measured an increase in the soil P supply not measured by the conventional 0.5 N NaHCO<sub>3</sub> extractant. Thus, the anion resin may have potential as a soil test method for rice soils. The potential of the anion resin as a research tool for characterizing P supply characteristics of flooded soil was illustrated in this study.

Considerable effort was devoted to experimentally explaining the greater amount of anion resin adsorbable P (ARAP) obtained from water-saturated soil relative to moist soil, because to do so might offer insight into the increased availability of P in flooded rice soils. Experiments showed that there was no increase in ARAP as iron became reduced. There was an increase in ARAP under waterlogged conditions when iron phosphate was added to soil, but the increase occurred before reducing conditions were obtained; as reducing conditions became evident as indicated by the presence of ferrous iron, no further increase in ARAP was observed. Reasons for not detecting an increase in ARAP upon reduction of these alkaline soils could be due to

(1) lack of reductant soluble soil P, (2) soil solution P being controlled by the calcium system so that P released during reduction had little effect on solution P concentration, or (3) inability of the anion resin to measure the increase in "available" P attributed to soil reduction. The third possibility does not seem likely, because the anion resin could adsorb P in the presence of iron in a water-saturated soil (Figure 3). The increase in ARAP in the water-saturated soil was attributed to the enhanced P diffusion brought about by a decrease in tortuosity, thus indicating that increased P availability upon flooding could be due to increased P diffusion.

A study of the effect of flooding on the capacity, kinetic, intensity, and diffusivity factors in the P supply process was undertaken to evaluate each factor in flooded soils. It was found that water-saturation and subsequent reducing conditions increased the capacity factor of the I-3 and La-2 soils, as measured by E-value, but had no definite influence on the capacity factor of the eight other soils. Reducing conditions per se did not increase the kinetic factor in nine of the ten soils studied, as measured by release of P from a soil to distilled water which served as a P "sink". Therefore, increased P availability upon flooding nine of the soils is not likely due to an increase in the kinetic factor. However, the kinetic factor of the acid La-1 soil did increase slightly on anaerobiosis; hence anaerobic conditions, associated with lowland rice soils, could explain a slight increase in P availability on flooding this soil.

Flooding may increase the intensity factor of acid soils, as evidenced by an increase upon flooding in the solution P concentrations of the three acid soils studied (I-7, NC-1, and La-1). However, flooding had essentially no measurable effect on the intensity factor of the seven alkaline soils of this study. Thus, increased P availability upon flooding of alkaline soils is not attributed to an increase in the intensity factor. The diffusivity factor, as measured by  $^{32}\text{P}$  self-diffusion coefficients, increased at least ten-fold upon water-saturation of soils that had moisture tensions greater than one-third bar.

Evaluation of experiments involving factors in the P supply from soil to root, revealed that the increase in the capacity, kinetic, and intensity factors upon flooding were slight and infrequent, while the increase in the diffusivity factor was pronounced and consistent. These data provide evidence that the increase in P availability upon flooding of soils is due primarily to an increase in the diffusivity factor.

Using a P fertilized soil and a minus P nutrient solution to nourish a split root system, with rice-shoot growth and P uptake as indicators of P availability, further evidence was obtained to support the hypothesis that increased soil moisture increased P availability through an enhancement of P diffusion. Due to the anaerobic conditions induced by water-saturation of the soil, all of the increase in P availability upon flooding the soil could not be attributed to an increase in P diffusion since anaerobic conditions may have increased the availability of reductant soluble P. In another split root system experiment, reduc-

tant soluble P was eliminated as a source of P by substituting the soil with P treated powdered cellulose which had a P diffusion coefficient similar to soil. Shoot growth and P uptake increased with moisture of the cellulose growth medium when low P solution concentration was the limiting factor in plant growth. In the cellulose, as in the soil, maximum growth was obtained in the water-saturated treatment where P diffusion rates were maximum. Increasing moisture did not increase plant growth when solution P concentration of the cellulose growth medium was sufficiently high so that even limited P diffusion could supply adequate P. The plant growth data are interpreted to indicate that essentially all of the increased P availability resulting from water-saturation of the cellulose was a result of an increase in the amount of P diffusing to the root surface. These data imply that the increase in P availability that occurs upon flooding a soil could be attributed to an increase in the diffusivity factor.

This study does not eliminate the possibility that reduction of iron or change in pH upon flooding may contribute to the increase in P availability in flooded rice soils. Nor does it eliminate the possibility that rice grown under flooded conditions has a lower functional P requirement or greater P absorptive capacity. However, all three approaches employed in this study do suggest that increased P availability upon flooding is due primarily to the pronounced increase in P diffusion that occurs upon flooding.

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