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Sorption and bioavailability of phosphorus during the drainage period of flooded-drained soils

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Summary Changes in P sorption and bioavailability were studied with 4 soils previously flooded and drained as occurs in rice-based cropping systems. Phosphorus sorption was measured at 15 and 119 days after drainage and the bioavailability of added and native soil-P was determined at 9, 16, 30, 45, 70 and 135 days in both flooded-drained and unflooded soils.

The P sorptivity and bonding energy of sorption increased under flooded-drained soil conditions. At 119 days after drainage the P sorptivity and bonding energy of sorption decreased as compared to 15 days after drainage. The P sorptivity of the flooded-drained soils, however, did not reach the same levels as existed in the soils prior to flooding. The bioavailability of P during the drainage period remained low and did not measurably change up to 70 days after drainage. At 135 days after drainage the bioavailability of P increased significantly, but did not reach the level found in the corresponding unflooded soils.

Introduction

Upland crops grown in rotation with flooded-rice culture have frequently been found to show poor growth due to induced P deficiency[2,5,6,7]. The chemical transformations of P that occur during soil flooding are very distinct. Crops grown in a previously flooded paddy soil often show severe P deficiency, while the soil formerly in the old levee positions, (above water line) which remains unsaturated during rice culture produces crops which grow normally. Soils undergoing this flooded-drained cycle have a higher content of amorphous iron and greatly increased P sorptivity than their unflooded counterparts[13]. The higher P sorptivity of the flooded-drained soils has been attributed to the high soil levels of amorphous iron[4].

When a flooded (anoxic) soil is drained, many of the physical and chemical conditions of the flooded soil are reversed, *i.e.*, oxygen enters the soil; the partial pressure of CO_2 decreases as entrapped CO_2 escapes; pH, which changes to values approaching neutrality during flooding tends to return to the level occurring in the soil prior to flooding, the chemical species that were reduced in flooded soil are reoxidized and the ionic strength of the soil solution decreases. All these changes lead to the precipitation and transformation of many chemical species including P, Fe, Al and Ca. The soil, immediately after the drainage, is therefore in the state of intense chemical instability. As the time period of soil drainage is increased, the instability decreases and the soil system gradually tends to equilibrate to the normal oxidized state. With increasing time after drainage, the freshly precipitated, highly amorphous materials particularly those containing Fe, tend to form relatively organized mineral forms which are less reactive with P.

The decrease in P sorptivity during the first few weeks of drainage is very rapid which is followed by a gradual decrease with time[13]. Willet and Higgins[12] noted a gradual decrease in acetate-extractable Fe and P sorptivity during a 21 month period of soil drainage. Even after 21 months of drainage, however, P sorptivity and acetate-extractable Fe in flooded-drained soil were much higher than its unflooded counterpart. Thus, it may take a long period of time, often up to 3 years as observed in field practice, for the P sorptivity to return to the level occurring in the soil prior to soil flooding.

The purpose of this study was to examine the changes in P sorptivity, energy of sorption and bioavailability of added and native soil-P as affected by the periods of soil drainage as occur in rice-based cropping systems.

Materials and methods

Four soils used for growing rice which exhibit P deficiency in rice-rotation crops were used in this study. The properties of these soils are reported in Table 1. Taxonomic classification of these soils are as follows: Sacramento clay: Fine, montmorillonitic, thermic, Vetric Haploaquoll; Stockton clay: Fine, montmorillonitic, thermic, Typic Pelloxerent; Meyers clay: Fine, Montmorillonitic, thermic, Entic Chromoxerent; Willows clay: Fine, Montmorillonitic, thermic, Typic, Pelloxerent. Sacramento and Stockton clay were collected from the areas having rice-upland crop rotations. In these areas, the fields are kept under flooded rice culture for 2–3 years followed by rotation crops such as corn, wheat, sorghum and safflower. Meyers clay was used for wheat and barley production and Willows clay was collected from a pasture land surrounded by rice fields. Meyers and Willows clay did not have the history of flooding and draining since brought under cultivation.

All four soils were incubated under flooded condition in 100-liter steel barrels lined with polyethylene bags. Between 10 and 15 cm water depth was maintained in the barrels for a 120 day flooding period. After 120 days, the flood water was siphoned out and the soil was allowed to drain. During the drainage period, the barrels were occasionally irrigated with distilled water to keep the soil moist (below field capacity). The soils were sampled 3 days before the indicated times for sorption and bioassay experiments. The sampled soils were allowed to air-dry under a stream of air at room temperature. The moisture content of a portion of air-dried soil was determined by oven-drying at 105°C. The P sorption data were later adjusted for the moisture content of the sample. The following experiments were conducted to meet the objectives of this study.

Effects of periods of drainage on P sorption

The P sorption studies were conducted in unflooded and flooded-drained soils at 15 days and 119 days after drainage. Duplicate samples of 2.0 g air-dry soil were weighed into 40 ml

Table 1. Properties of soils used

Soil	Unflooded soils			Flooded-drained soils		
Soil:Water ratio	Saturated paste	1:1 pH	1:10		1:1	1:10 pH
(a) pH						
Sacramento clay	6.32	6.37	6.74		6.45	6.75
Stockton clay	5.18	5.34	5.74		5.30	5.67
Meyers clay	6.92	7.10	7.47		7.29	7.64
Willows clay	6.84	6.94	7.40		6.45	6.94
Soil	**Total P**	**Organic P**	**Al-P**	**Fe-P**	**Ca-P**	**RS-P**
(b) Phosphorus status (μgP/g soil)						
Sacramento clay	596.8	41.5	59.0	100.8	202.8	84.4
Stockton clay	260.1	35.6	44.9	56.4	10.6	40.4
Meyers clay	344.3	53.3	36.6	51.8	82.1	90.4
Willows clay	550.0	106.7	54.2	121.9	132.8	158.0
Soil texture class	**Sand %**	**Silt %**	**Clay %**	**CEC cmol (p +) kg^{-1}**		**Organic carbon %**
(c) Texture, CEC and organic carbon						
Sacramento clay	7	35	58	53.5		1.94
Stockton clay	15	33	52	53.1		1.27
Meyers clay	17	39	44	45.4		0.78
Willows clay	14	38	48	48.9		1.38

centrifuge tubes. Thirty ml of 0.01 *M* $CaCl_2$ solution containing 10, 15, 20 and 25 ppm P as $Ca(H_2PO_4)_2 \cdot H_2O$ and two drops of toluene were added to the tubes. The P amended soils in the tubes were incubated at 20°C for 4 days with shaking for 5 minutes each day. At the end of incubation the tubes were again shaken for 15 minutes, centrifuged at 25000 revolutions per minute for 15 minutes and the supernatant liquid was decanted. The decanted liquid was filtered and P in the solution was determined by the method of Watanabe and Olsen[11]. The amount of P not accounted for in the solution was considered to be sorbed. The P sorption data were fitted to a Langmuir isotherm and bonding energy of adsorption was calculated. The effects of periods of soil drainage on the bonding energy and P sorption were evaluated.

Effects of periods of drainage on the bioavailability of P

The bioavailability of native soil-P as affected by periods of drainage was determined by assaying the flooded-drained soils by the method of Stanford and DeMent[10]. The flooded-drained soils were assayed at 9, 16, 30, 45, 70 and 135 days after drainage. Unflooded soils were also used for comparison. The bioassay involved three steps:

(1) Growing the test plants: Wheat (*Triticum aestivum*) cv. Anza was the test crop.

Test plants were grown in 500 ml plastic containers that could nest into one another. A bottomless container was nested in another containing acid and water washed sand. Seventy wheat seeds were sown in each container which was irrigated with distilled water and placed in an illuminated growth chamber with day and night temperatures 20°C and 15°C, respectively.

After 10 days the wheat plants were thinned to 60 per container. At age of 14 days from seeding, the wheat roots were intermeshed in the sand and coiled at the bottom of the outer container (with bottom) so that the seedlings in sand in the bottomless inner container could be placed directly on the soil being evaluated.

(2) Assaying the soil: The bioavailable P in the soil was assayed by nesting the seedlings grown in the acid washed sand (step 1) over the test soil and allowing growth for 9 days. In

each assay the soils were treated with 0, 25 and 100 ppm P as $Ca(H_2PO_4)_2 \cdot H_2O$. The P fertilizer was dissolved in water and sprayed on the soil while mixing to provide uniform distribution. A common application of 60 ppm N as urea and 40 ppm K as KCl was also used for each treatment. The moisture content of the soil was brought to 25% by weight. The N, P and K amended soils at 25% moisture, equivalent to 300 g dry weight of soil, were potted in the plastic containers and nested with the 14 days old wheat seedlings (step 1). The soils were assayed in a growth chamber for 9 days with irrigations at 4 and 7 days to keep the soil moist. The day and night temperatures of the growth chamber were 20°C and 15°C, respectively. At the end of the assay period, the wheat seedling were harvested from the surface of the sand, washed with distilled water and dried to constant weight at 70°C.

(3) Analysis of the test plants: Plant samples of 0.10 g ground to 20 mesh were weighed into 50 ml digestion tubes and digested with HNO_3 on a hot plate. The P concentration in the digested samples was determined by the ascorbic acid method of Watanabe and Olsen[11]. From the P concentration in the digested solution, P uptake was calculated. The P uptake data as a function of the periods of drainage were plotted for different levels of P. The mean response to P application was also plotted and the response functions were calculated.

Results and discussion

The experimental results show that the period of soil drainage had marked effects on the sorption and the bioavailability of P. Initially P sorption and bioavailability did not change. At about 119 days after drainage, however, P sorption and the bonding energy of adsorption decreased as compared to recently drained soils. They did not, however, reach the level of the unflooded soils. Bioavailability of native soil-P or added fertilizer-P also increased at about 135 days after drainage. The wheat on flooded-drained soils responded to added fertilizer-P at all times after drainage. This verifies field trials where with adequate P application, satisfactory crop yield can be obtained in flooded-drained soil[2].

Effects of the periods of drainage on P sorption

Phosphorus sorption, in all the soils, was lowest under unflooded conditions, and increased at 15 days after drainage (Table 2, Fig. 1 and 2). At 119 days after drainage, P sorption decreased significantly as compared to 15 days. It did not, however, return to the original levels of P sorption in the unflooded soils. The slopes of the P sorption isotherms (Figs. 1 and 2) show the rate of increase in P sorption at different periods after draining as a function of equilibrium P concentration (Ce) in two selected soils. The slopes decreased as the period after drainage increased. Sacramento and Stockton clay had previously been used for flooded rice culture and these two soils will be referred to as 'rice soils' in the following discussion. Meyers and Willows clay did not have the history of flooding and draining and are referred to as 'non-rice' soils.

Table 2. Effects of periods of drainage on equilibrium P concentration (Ce) at selected Pe values

Soils/Pe	15 days after drainage	119 days after drainage	Unflooded soil
		Ce in μgP/ml	
Sacramento clay			
Pe = 10 ppm	0.079	0.286	0.664
Pe = 25 ppm	1.830	4.919	5.915
Stockton clay			
Pe = 10 ppm	0.048	0.070	0.199
Pe = 25 ppm	2.720	3.009	3.739
Meyers clay			
Pe = 10 ppm	0.675	1.092	2.179
Pe = 25 ppm	5.681	7.472	9.346
Willows clay			
Pe = 10 ppm	0.285	0.371	1.047
Pe = 25 ppm	3.535	4.645	7.540

Pe = P added in external solution (μg P/ml).

The effect of period of drainage on Ce (equilibrium P concentration) at two external P concentrations (Pe) is shown in Table 2. At any Pe value, the Ce increased by 2 to 8 times, depending on soil, as the period after drainage increased from 15 to 119 days. The two non-rice soils maintained much higher Ce values at any Pe (Table 2) and the P sorption

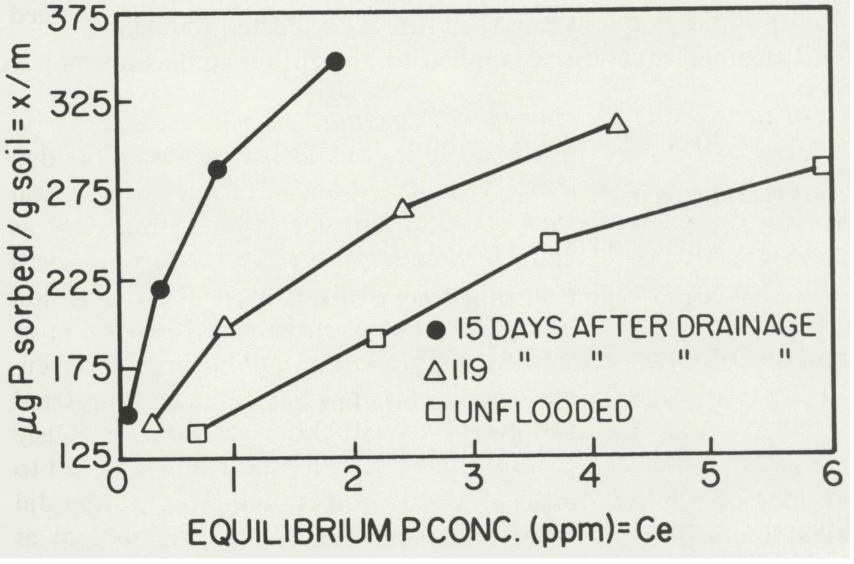

Fig. 1. Effects of periods of drainage on P sorption in Sacramento clay.

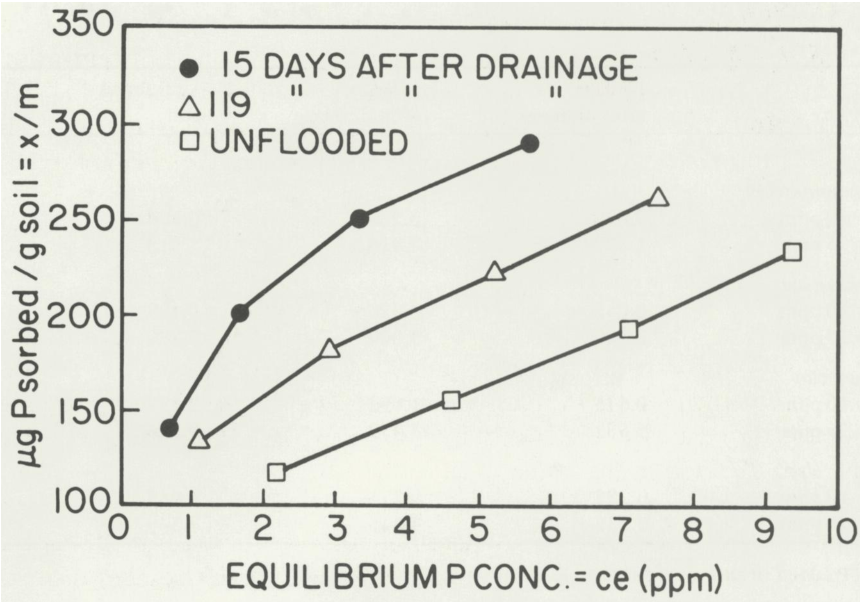

Fig. 2. Effects of periods of drainage on P sorption in Mayers clay.

in these soils was much lower than the rice soils. Even upon flooding and draining, the two non-rice soils maintained a higher P concentration than the two rice soils. It is likely that due to several cycles of flooding and draining highly ordered iron oxides in the rice soils changed to amorphous iron oxides with high surface area capable of P sorption[4]. The P sorption in rice soils can, therefore, be expected to be high.

The Langmuir equation, as applied to absorption studies in soil is as follows:

$$X/m = (abCe)/(1 + bCe) \quad (1)$$

It was rearranged as

$$1/(X/m) = (1/a) + (1/ab)(1/Ce) \quad (2)$$

X/m = μg P adsorbed per g of soil.

a = Adsorption maximum

b = A constant related to bonding energy of adsorption.

Ce = Equilibrium P concentration, μg/ml

The plot of $1/(X/m)$ versus $1/Ce$ according to equation 2 results in a straight line with y-intercept = $1/(a)$ and slope = $1/ab$.

The P sorption data were fitted to the Langmuir isotherm. The data on all soils except Stockton clay fitted reasonably well to the Langmuir isotherm. In Stockton clay, the Ce's at the external P concentration (Pe) of 10 ppm were very small. Therefore, the inverse of Ce in 1/Ce *versus* 1/(X/m) plot, yield high values. After excluding the Ce's at Pe = 10 ppm from the regression analysis, the data fitted better to the Langmuir isotherm.

The constant b values, related to the bonding energy of adsorption were significantly affected by the soil type and the period of drainage (Table 3). The Langmuir constant b was the highest with Sacramento clay followed by Stockton clay, an acidic soil. The constant b for the Meyers clay was the lowest. The values of b for the two non-rice soils were much lower than for the two rice soils. This indicates, assuming that sorption can be explained by Langmuir isotherm, that the rice soils sorb P much more strongly than the non-rice soils. The values of the Langmuir constant b were the highest at 15 days after drainage and decreased as the period of drainage increased, with the minimum being in unflooded soils. The higher amount of energy associated with P adsorption in recently drained soil can be expected to lower the P desorption and the available P concentration in soil during crop growth. The relationship of bonding energy (b) with P sorption as affected by soil type and period of drainage is shown in Fig. 3. The increase in P sorption per unit increase in b was the highest in Meyers clay followed by Willows and Sacramento clay. Therefore, a change in the value of b will not be an indicator of P sorption.

Table 3. Effects of period of drainage on the magnitude of Langmuir constant b for bonding energy

	Days after drainage		
Soil	15	119	Unflooded
1. Sacramento clay	10.8	3.2	1.4
2. Stockton clay	7.05	2.21	1.05
3. Meyers clay	1.13	0.82	0.30
4. Willows clay	2.86	2.42	0.83

Effects of periods of drainage on bioavailability of P

The overall mean P uptake by wheat seedlings was relatively unchanged for 70 days, but at 135 days after drainage, it increased over earlier periods of drainage (Fig. 4). The increase in P uptake at 135 days after drainage over drainage periods was about 20%. The plant P uptake in unflooded soil was the highest and was more than that at 135 days after drainage.

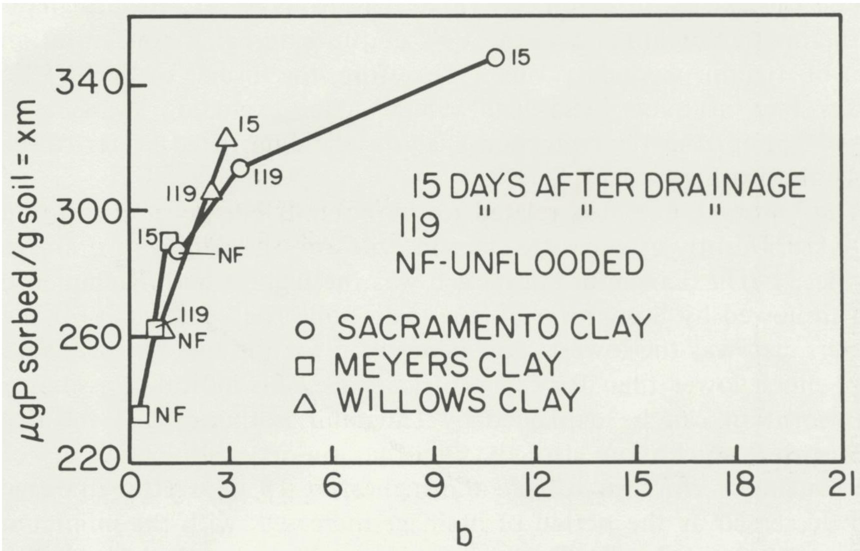

Fig. 3. Relationship among Langmuir constant, b, periods of drainage and x/m at Pe-25 ppm.

At the 3 levels of P application studied, the trends of the mean change in P uptake as a function of the drainage period were similar (Table 4). The P uptake by wheat during the first 70 days after drainage did not change with time. At 135 days after drainage, the P uptake increased. However, the P uptake in unflooded soil was generally greater than in flooded-drained soils even at 135 days after drainage. In some cases the P uptake at 9 days after drainage was greater than at other periods during the first 70 days. The 9 day period after drainage however is generally too short a time to reoxidize the clay soil completely since the soil has a high water-retention capacity. It appears that the increased amount of P made available during the flooding period was not completely immobilized during the 9 day period after drainage. Since the soils were assayed with established and P-starved plants with a well established root system, any P not immobilized during the drainage period would be quickly used by the plants. The increased P uptake at 9 days after drainage suggests that the advantage of flooding on P availability still persisted due to incomplete reoxidation and a relatively short period for the P to be immobilized.

Effects of periods of drainage on P uptake in different soils

Meyers clay maintained the highest and Stockton clay the lowest plant P uptake throughout the drainage period. Generally no difference in P uptake between Sacramento and Meyers clay occurred during the

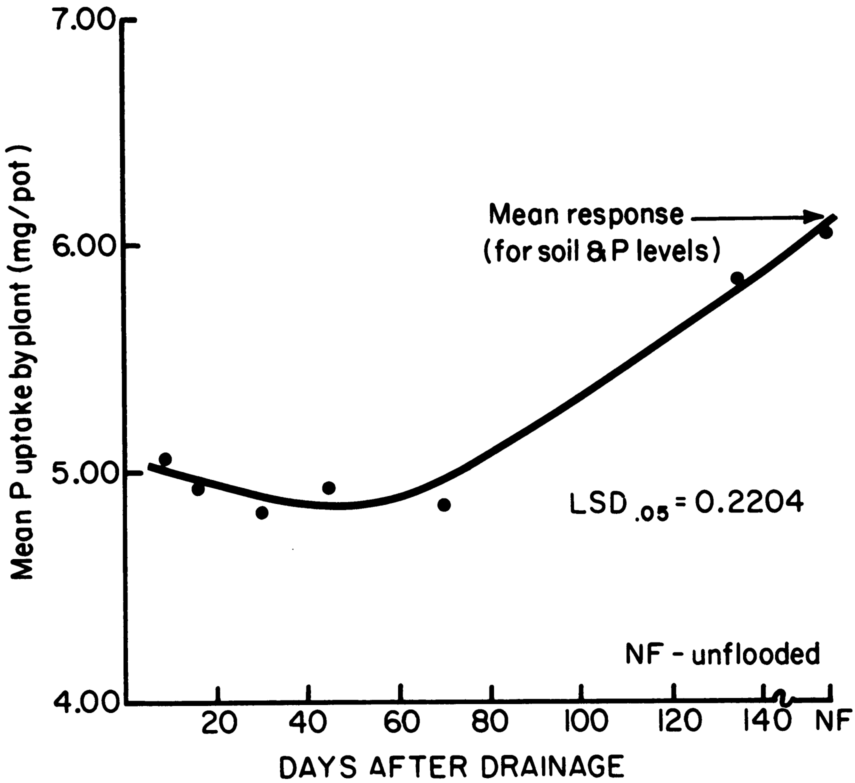

Fig. 4. Effects of periods of drainage on overall mean P uptake.

drainage period (Table 4). The P uptake in Willows clay was generally lower than predicted based on its P sorption characteristics (Table 2) and its ability to maintain solution P concentration as shown in kinetic studies[8, 9]. The wheat seedlings generally showed poor root development in this soil during the bioassay period due to its salt and clay content. Willows clay was initially collected from an area surrounded by fields under flooded rice culture. Such areas often develop salinity due to an elevated water table. The Willows clay used in the present study had the electrical conductivity of saturated extract of soil (EC_e) value of $1.6\ S\,m^{-1}$ which is high for optimum wheat growth. According to Ayers and Westcot[1] the EC_e value of $0.6\ S\,m^{-1}$ or less is normal for wheat, while at $EC_e = 1.3\ S\,m^{-1}$ yield decreases by 50% and at $EC_e = 2.0\ S\,m^{-1}$ crop growth ceases completely. Elevated salinity was the most important reason for poor growth of wheat seedlings. The inability of wheat to grow properly caused a low P uptake in Willows clay. On an overall basis, the P uptake was the highest in Meyers clay which

Table 4. Effects of periods of drainage and P levels on bioavailability of P in 4 soils

		P uptake (mg/pot) Days after soil drainage						
Soil	P level (ppm)	9	16	30	45	70	135	Unflooded
Sacramento clay	0	4.958	4.284	4.208	4.295	4.327	5.285	5.338
	25	5.215	4.805	4.996	5.162	4.581	5.243	5.518
	100	6.111	6.038	5.922	5.535	5.371	7.148	7.699
	Mean	5.428	5.042	5.042	4.997	4.760	5.892	6.185
Stockton clay	0	4.665	3.985	3.797	4.299	3.628	4.960	4.525
	25	5.101	4.245	4.315	4.467	4.457	5.046	5.484
	100	5.845	4.923	4.880	5.407	6.096	6.729	7.349
	Mean	5.204	4.384	4.331	4.724	4.727	5.578	5.786
Meyer clay	0	4.839	3.971	4.186	4.378	4.508	5.428	5.099
	25	5.157	4.922	5.179	4.818	4.701	5.746	5.488
	100	6.174	6.674	6.620	6.654	6.882	7.185	8.313
	Mean	5.390	5.189	5.328	5.283	5.363	6.120	6.300
Willows clay	0	4.992	4.776	4.017	4.282	3.976	4.799	4.699
	25	4.694	4.973	4.179	4.913	4.849	5.589	5.918
	100	5.663	5.662	5.142	5.206	4.921	6.922	6.537
	Mean	5.116	5.137	4.446	4.800	4.582	5.770	5.718

Comparisons	$LSD_{0.05}$ mg/pot
1. Between periods of drainage	0.2204.
2. Between soils	0.1668.
3. Between P levels	0.1444.
4. Between periods of drainage for the same soil or *vice versa*	0.4407.
5. Between periods of drainage for the same P level or *vice versa*	0.3816.
6. Between soils for the same P level or *vice versa*	0.2885.
7. Between the levels of a factor for a given level of remaining two factors	0.7633.

was better than in Sacramento clay at 95% level of confidence (Table 4). The P uptake in Stockton and Willows clay were not different. The P uptake by wheat in these two soils was, however, lower than Sacramento and Meyers clay.

The overall response of wheat to P (averaged over drainage periods) was linear in all the soils except Willows clay (Fig. 5). The rate of increase in P uptake due to the application of P-fertilizer was the largest (0.023 mg P per ppm P applied) in Meyers clay. The rates in Stockton and Sacramento clay were similar. In terms of the mean amounts of P uptake by wheat, there was no difference among Sacramento, Meyers and Willows clay at 0 and 25 ppm P but the P uptake from Stockton clay was lower (Table 4). At 100 ppm P, however, wheat growth and P uptake was greatest on Meyers clay which was better than Sacramento clay which in turn was better than the other two soils. Over the entire range of P application, the P uptake from Meyers clay was the highest and from Stockton clay the lowest. The overall mean P uptake increased from 4.522 mg/pot to 4.987 mg/pot (10.3% increase) and 6.200 mg/pot (37.1% increase) due to application of 25 and 100 ppm P respectively (Table 4). In all 4 soils, the effect of

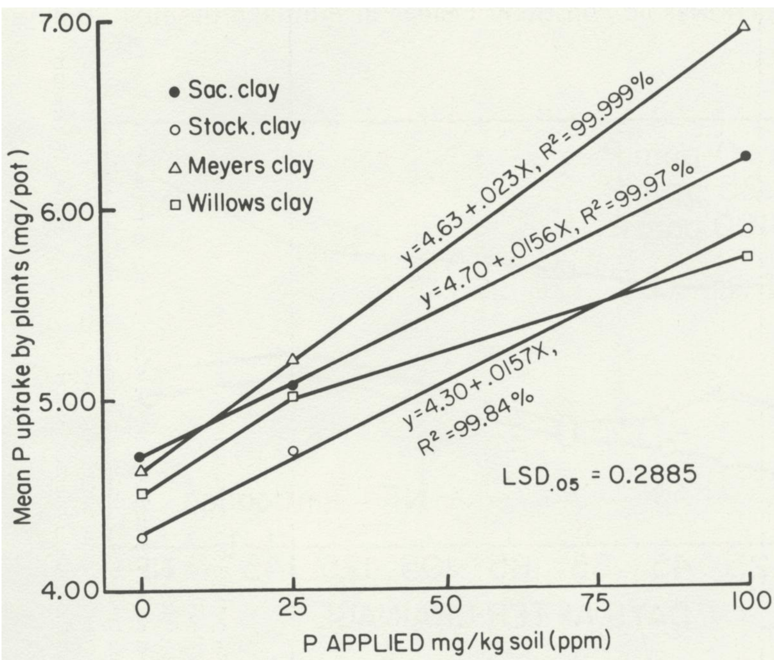

Fig. 5. Effects of soil type and P level on mean P uptake.

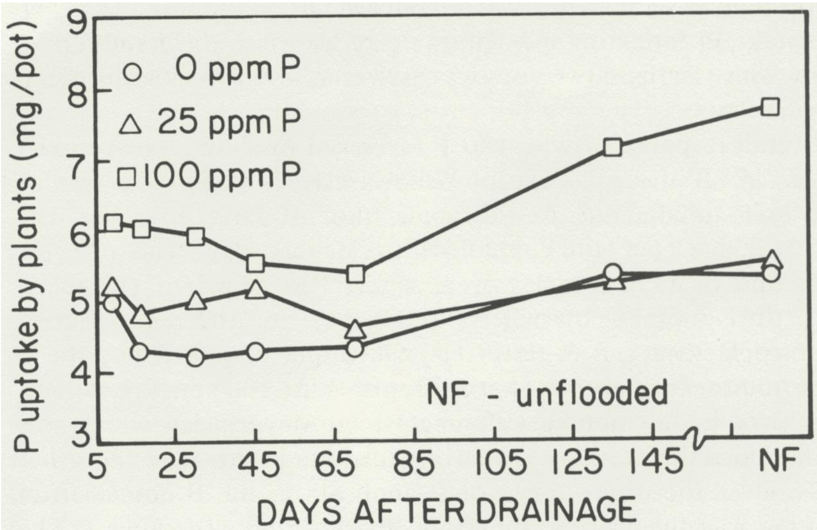

Fig. 6. Effects of periods of drainage on P uptake in Sacramento clay.

P application on P uptake was measurable at all periods of drainage (Table 4, and Figs. 6–7). In all soils, the P uptake increased at 135 days although there was no consistent change in P uptake the first 70 days of drainage.

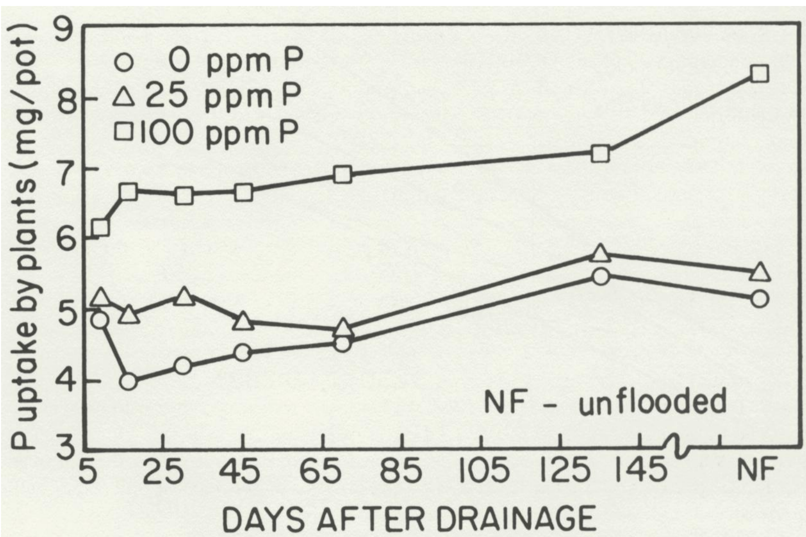

Fig. 7. Effects of periods of drainage on P uptake in Meyers clay.

Relationship between P sorption and bioavailability of P

This study indicates that P sorption decreased in drained soils up to 119 days. This is roughly the same period at which the bioavailability of P also increased. The study indicated that although the P sorption in soil decreased at 119 days, it did not reach the level found in the unflooded soil. The bioavailability of P also reflected the same trend.

The present study indicates that the bioavailability of added and native P can be related through soil P adsorption. Wheat responded to P and its uptake was increased by adequate P fertilization applied at any time during the drainage period. Heritage[3] also found that an adequate application of P fertilizer, which provides a minimum P concentration of 0.13 ppm in both flooded (rice bay) and unflooded (rice bank) soils, eliminated differences in seedling growth of maize grown in flooded-drained soil. There is an apparent advantage in delaying the planting of crops for 4–5 months after drainage, to allow reduction in soil sorptivity when P fertilizer requirements are reduced significantly.

The increased P sorptivity resulting from flooding and draining of soil tended to decrease with increasing periods of soil drainge. The bioavailability of P also increased after a threshold period of about 4 months after soil drainage. Adequate P fertilization increases the bioavailability of P when applied at any time after soil drainage.

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