

Phosphorus Sorption Pattern Under Controlled Redox Potential For Crowley Silt Loam Soil

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Key words: Phosphorus sorption; redox potential; reduction process; monocalcium phosphate; serum cap; centrifuge bottle; magnetic stirrer.

RINGKASAN

Empat sampel tanah Crowley bertekstur lom berkeleodak ditimbang dan dimasukkan ke dalam kelalang yang bawahnya rata berisipadu 2 liter. Sesudah dimasukkan 0.4% jerami padi yang sudah dikisar, 0.01 M CaCl₂ dicampurkan ke dalam tiap-tiap kelalang dan campuran ini sentiasa dikacau dengan pengacau magnet untuk menubuhkan keadaan pengoksidaan dan penurunan. Untuk mendapatkan nilai Eh pada aras -220 mv, gas nitrogen hendaklah dimasukkan berselantaran selama 13 hari. Bagi keadaan pengoksidaan pula, udara biasa dimasukkan ke dalam kelalang tersebut. Dua kadar P (10 bsj dan 100 bsj) di dalam bentuk Ca(H₂PO₄)₂H₂O dimasukkan ke dalam campuran tanah.

Didapati pH tanah yang dioksidakan tidak berubah di sepanjang percubaan ini manakala tanah yang diturunkan, nilai pHnya bertukar daripada 5.5 ke arah neutral. Lebih banyak P terjerap di dalam keadaan penurunan daripada keadaan pengoksidaan. Walaubagaimanapun, kesan ini lebih jelas apabila kadar P meningkat. Selepas 288 jam, nilai jerapan P adalah 55.9% di dalam keadaan pengoksidaan dan 90.2% di dalam keadaan penurunan. Untuk 10 bsj P yang digunakan, jerapan maksimum didapati selepas dua hari pembajaan manakala pada kadar 100 bsj pembajaan P, graf menjadi rata selepas enam hari.

SUMMARY

Four samples of Crowley silt loam soil were weighed into a 2-liter flat-bottomed flasks. After the introduction of 0.4% ground rice straw, 0.01 M CaCl₂ were added in each flask and the mixture stirred constantly by a magnetic stirrer to establish oxidized and reduced conditions. It took 13 days of continuous purging with nitrogen gas to obtain an Eh value of -220 mv. For the oxidized condition ordinary atmospheric air was bubbled into the flasks. Two levels of P (10 ppm and 100 ppm) in the form of Ca(H₂PO₄)₂H₂O was applied to the soil mixture.

It was found that the pH of the aerated treatment remained rather constant throughout the entire investigation whereas in the reduced ones the pH increased from 5.5 to neutrality. More P was adsorbed under the reduced condition than the oxidized ones. However, the effect was much more pronounced at the higher level of P fertilization. After 288 hours there were 55.9% and 90.2% adsorption of P in the oxidized and reduced conditions respectively. For 10 ppm P the maximum adsorption was obtained after a two-day period whereas for 100 ppm P. The graph levelled off after six days.

INTRODUCTION

Some of the factors that govern the sorption and release of added and native soil P are Eh, pH, soil characteristics, temperature and microbiological activity. Several investigators have shown that when soil is flooded continuously a reduced condition is established within a few days (Acmine,

1962; Redman and Patrick, 1964; Ponnampereuma, 1965; Mahapatra, 1968, Husin *et al.* 1979). Flooding brings about an increase in extractable phosphorus mainly by reduction of ferric to ferrous phosphate and hydrolysis of ferric and aluminium phosphate (Tsubota, 1959; Husin *et al.* 1979).

Key to author's name: A. Husin

The objectives of this experiment were twofold. Firstly, to investigate the optimum time needed for maximum sorption of P after its addition under controlled Eh condition. Secondly, to investigate the sorption pattern of added phosphorus when different concentrations of phosphorus (10 and 100 ppm P) were applied under naturally oxidized and naturally reduced conditions.

MATERIALS AND METHODS

A total of four 300 g samples of Crowley silt loam soil which had been ground to pass a 20-mesh sieve were transferred into 2-liter flat-bottomed flasks to establish the following conditions:

- A. Oxidized with 10 ppm P added
- B. Reduced with 10 ppm P added
- C. Oxidized with 100 ppm P added
- D. Reduced with 100 ppm P added

The system described by Patrick *et al.*, (1973) was used to establish these conditions.

To each flask about 0.4% ground rice straw was added to act as a source of energy for the soil microbes to hasten the reduction process. Then, 1475 ml of 0.01 M CaCl₂ was added to each flask. All the necessary electrical connections, regulators, inlet and outlet valves were made for measuring the Eh and pH values. The flasks were made airtight especially for the reduced condition.

The soil was incubated and stirred for 13 days till the Eh reading was steady at the required values (-220 mV for reduced condition and +660 mV for oxidized condition). For the reduced samples, nitrogen gas was bubbled continuously into the flask. For the oxidized samples, ordinary air was bubbled into the flask.

Table 1 shows the changes in pH and Eh with time under different environmental conditions. Initially all the pH values were the same, having a pH value of 5.50. After some time, the pH of the oxidized condition decreased steadily to 5.10 while the pH of the reduced condition increased steadily to 6.85 in the 10 ppm flask and 6.35 in the 100 ppm flask.

At the same time some changes took place in the oxidation reduction potentials (Eh). The Eh of the oxidized conditions increased to +660 mV whereas the Eh for the reduced conditions decreased to -220 mV by the end of the thirteenth

day. These values were controlled and maintained for the entire experiment by the help of the meterally which regulated the inflow of nitrogen and atmospheric air in the reduced and oxidized flasks respectively.

Soil moisture ratio was determined by gravimetric method. A two 30 ml sample was siphoned from each flask and the amount of moisture determined. This determination was necessary for the computation of P adsorbed to the soil colloids. For the aerobic condition the values were 6.23 : 1 for both the treatments while for the anaerobic condition the values were 6.12 : 1 and 6.32 : 1 for the 10 ppm P and 100 ppm P added respectively.

When the Eh was stable at the required value, four 45-ml samples of the soil suspensions were taken to determine the P status in the soil. Then a phosphorus equivalent to 10 ppm and 100 ppm P in 25 ml of distilled water was added to the respective flasks. An equivalent of 15 mg P for 10 ppm treatment, and an equivalent of 150 mg P for the 100 ppm treatment were added in the form of monocalcium phosphate Ca(H₂PO₄)₂·H₂O to the respective flasks.

Duplicate 45 ml samples of the soil suspensions were taken at different time intervals from each flask : 0.25 hr, 1 hr, 3 hr, 6 hr, 12 hr, 24 hr, 48 hr, 96 hr, 144 hr, 192 hr and 288 hr.

In the treatment of reduced samples, a 45 ml sample was taken through the serum cap with a syringe. The sample was quickly transferred into an air-tight centrifuge bottle which had been purged with nitrogen. It was centrifuged at 5,000 rpm for 30 minutes after which it was filtered with suction through a 5.5 cm Whatman number 42 filter paper. The filtered supernatant was analysed for water soluble P.

The P in the solution was analysed using the method of Watanabe and Olsen (1965). The difference between the P concentration added at zero time and the water soluble P was considered to be the amount of adsorbed P. The percentage of the P adsorbed was calculated.

RESULTS AND DISCUSSION

The results of the investigation are presented in Tables 2 to 5 and shown in Figures 1 and 2.

The Phosphorus Sorption Isotherm for the 10 ppm P Addition

The adsorption of P to the soil colloids took place very quickly (Tables 2 and 3).

PHOSPHOROUS SORPTION UNDER CONTROLLED REDOX POTENTIAL OF CROWLEY SILT

TABLE 1

The pH and Eh Readings for the Oxidized and Reduced Conditions of Crowley Silt Loam Soil Before and After the Addition of 10 ppm and 100 ppm P (The Eh Reading is the Value After Correcting it with Quinhydrone at pH 4.01 at 30°C. The Eh Electrodes Standardised by Quinhydrone Using pH 4.01 Buffer at 30°C = 220 mv)

Date	Oxidized 10 ppm		Oxidized 100 ppm		Reduced 10 ppm		Reduced 100 ppm	
	pH	Eh	pH	Eh	pH	Eh	pH	Eh
1/7	5.50	+270	5.50	+270	5.50	+270	5.50	+270
4/7	5.15	+640	5.25	+620	5.88	+ 80	5.80	+150
5/7	5.15	+650	5.30	+620	6.00	+ 55	5.90	+130
6/7	5.20	+650	5.70	+640	6.15	+ 85	6.00	+ 70
7/7	5.20	+680	5.30	+660	6.10	+ 50	5.30	+ 70
8/7	5.20	+690	5.20	+660	6.05	+ 20	5.65	+ 20
9/7	5.20	+665	5.20	+665	6.15	- 10	5.70	- 30
10/7	5.20	+660	5.20	+640	6.25	- 20	5.90	- 70
11/7	5.15	+650	5.20	+640	6.30	- 40	6.20	-110
12/7	5.10	+645	5.15	+620	6.15	-120	6.35	-190
13/7	5.10	+665	5.15	+665	6.40	-170	5.95	-200
14/7	5.10	+635	5.15	+650	6.55	-200	6.70	-205
15/7	5.15	+640	5.15	+665	6.80	-205	6.90	-220
16/7	5.10	+650	5.15	+665	6.80	-210	6.95	-220
17/7	5.10	+650	5.15	+670	6.85	-220	7.00	-220
18/7	5.10	+670	5.15	+660	6.40	-220	6.80	-220
19/7	5.10	+670	5.15	+660	6.80	-220	6.40	-220
20/7	5.10	+660	5.15	+660	6.80	-220	6.50	-210
21/7	5.10	+660	5.10	+660	6.75	-220	6.50	-220
22/7	5.10	+660	5.10	+660	6.85	-220	6.35	-220

The amount of P adsorbed from zero time till the second day showed some difference between the aerobic and anaerobic conditions. After 15 minutes, 27.04 ppm P was adsorbed in the oxidized condition and 47.71 ppm P in the reduced condition which represent 43.40% and 77.96% adsorption respectively. However, after 48 hours, the graph began to plateau, and the values of the aerobic as well as the anaerobic samples began to come close to one another with 93.42% adsorption in the oxidized condition and 91.74% adsorption in the reduced condition, which were equivalent to 58.12 ppm P and 57.37 ppm P respectively. From 48 hours onwards, the % adsorptions of P were close to one another and the % difference between the two treatments did not differ by more than 1.7%.

At the lower rate of P addition in the aerobic condition, the statistical analysis indicated that a significant P sorption took place from the time P was added up to 12 hours later. From that point onwards, the graph began to level off. On the other hand the anaerobic condition showed a significant change from zero time up to 3 hours later. Beyond the 3-hour interval the increase in P sorption was no longer significant.

The Phosphorus Sorption Isotherm for the 100 ppm P Addition

The reduced and oxidized samples of the 100 ppm P had a somewhat different pattern. First, the overall percentage adsorption was much lower than when 10 ppm P was added, especially for the oxidized condition. By 48 hours only 33.82% of

TABLE 2

Adsorption of P at Various Time Intervals when
10 ppm P was
Added to an Oxidized Crowley Silt Loam Soil

Time in hours	Solution P ($\mu\text{g}/\text{ml}$)	(1) Adsorbed P ($\mu\text{g}/\text{g}$)	(2) % Adsorption
0	10.00	—	—
0.25	5.66	27.04	43.4 a
1	3.89	38.07	61.1 b
3	2.29	48.03	77.1 c
6	1.84	50.84	81.6 cd
12	1.37	53.76	86.3 de
24	0.83	57.13	91.7 e
48	0.66	58.19	93.4 e
96	0.52	59.06	94.8 e
144	0.45	59.50	95.5 e
192	0.41	59.75	95.9 e
288	0.33	60.24	96.7 e

(1) Ratio of moisture : Soil = 6.23 : 1

(2) Values with the same letters are not significantly
different ($P \leq 0.01$)

TABLE 3

Adsorption of P at Various Time Intervals when
10 ppm P was
Added to a Reduced Crowley Silt Loam Soil

Time in hours	Solution P ($\mu\text{g}/\text{ml}$)	(3) Adsorbed P ($\mu\text{g}/\text{g}$)	(4) % Adsorption
0	10.0	—	—
0.25	2.20	47.74	78.0 a
1	1.37	52.82	86.3 ab
3	1.08	54.59	89.2 b
6	0.86	55.94	91.4 b
12	0.58	57.65	94.2 b
24	0.58	57.65	94.2 b
48	0.63	57.34	93.7 b
96	0.50	58.14	95.0 b
144	0.50	58.14	95.0 b
192	0.58	57.65	94.2 b
288	0.48	58.26	95.2 b

(3) Ratio of moisture : Soil = 6.12 : 1

(4) Values with the same letters are not significantly
different ($P \leq 0.01$)

TABLE 4

Adsorption of P at Various Time Intervals when
100 ppm P was
Added to an Oxidized Crowley Silt Loam Soil

Time in Hours	Solution P ($\mu\text{g}/\text{ml}$)	(5) Adsorbed P ($\mu\text{g}/\text{g}$)	(6) % Adsorption
0	100.00	—	—
0.25	92.73	45.29	7.27 a
1	90.56	58.81	9.44 ab
3	87.75	76.32	12.25 abc
6	81.33	116.31	18.67 bcd
12	77.38	140.92	22.62 cd
24	71.99	174.50	28.01 de
48	66.18	210.70	33.82 ef
96	58.71	257.24	41.29 fg
144	48.96	317.98	51.04 gh
192	48.75	319.29	51.25 gh
288	44.08	348.38	55.92 h

(5) Ratio of moisture : Soil = 6.23 : 1

(6) Values with the same letters are not significantly
different ($P \leq 0.01$)

TABLE 5

Adsorption of P at Various Time Intervals when
100 ppm P was
Added to a Reduced Crowley Silt Loam Soil

Time in Hours	Solution P ($\mu\text{g}/\text{ml}$)	(7) Adsorbed P ($\mu\text{g}/\text{g}$)	(8) % Adsorption
0	100.00	—	—
0.25	72.86	171.56	27.14 a
1	65.11	220.50	34.89 ab
3	59.92	253.31	40.08 bc
6	48.89	323.02	51.11 d
12	40.62	375.28	59.38 de
24	34.90	413.33	65.10 ef
48	28.58	451.37	71.42 fg
96	15.87	531.70	84.13 h
144	8.32	579.42	91.68 h
192	9.75	570.38	90.25 h
288	9.80	570.06	90.20 h

(7) Ratio of moisture : Soil = 6.32 : 1

(8) Values with the same letters are not significantly
different ($P \leq 0.01$)

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the P added was adsorbed in the aerated soil while in the reduced condition 71.42% adsorption took place. Only after 144 hours did the graph begin to level off in both the oxidized and reduced conditions with values of 51.04% and 91.68% adsorption respectively. By 288 hours, only 55.92% adsorption had taken place in the oxidized samples compared to 90.20% for the reduced ones (Figure 1). The difference in percentage P adsorption between the aerobic and anaerobic conditions ranged from as low as 19.88% to as high as 42.84%. By the end of the twelfth day the % P sorption for the higher rates of P fertilization was 55.9% and 90.2% in the oxidized and reduced conditions respectively.

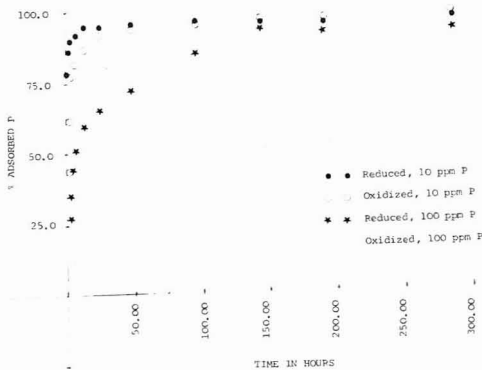


Fig. 1 The Phosphorus Sorption Isotherm for Crowley Silt Loam Soil Under Controlled Redox Potential at two levels of Added Phosphorus

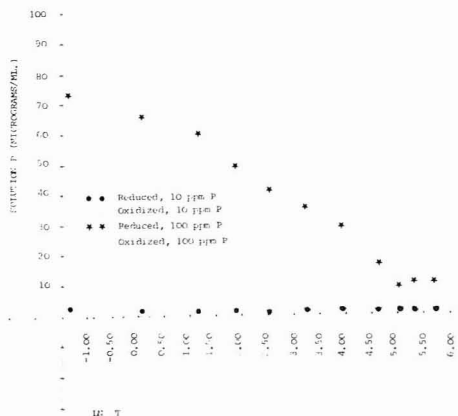


Fig. 2 Phosphorus Sorption Isotherm for Crowley Silt Loam Soil Under Oxidized and Reduced Conditions.

For the oxidized condition, there was no well defined point where the graph levelled off. The amount of P sorbed kept increasing with time. For the reduced condition, on the other hand, the graph levelled off after 48 hours up to the end of the study.

Figure 1 shows the % P sorption for both treatments under oxidized and reduced conditions at the various time intervals. None of the equations suggested by Chien *et al.*, (1980) could transform the above set of data into a linear fashion. Nevertheless, using the Elovich equation, the data were transformed as shown in Figure 2.

CONCLUSION

The experiment showed that if the amount of added P is small (10 ppm), most of it will be adsorbed into the soil colloids at an inconsistent rate during the first 24 hours. After 24 hours, however, the added P is adsorbed at a fairly consistent rate. When a larger amount of P is added (100 ppm) adsorption in the reduced condition will be greater, irrespective of the time span. The greater P sorption is probably due to the greater surface area becoming exposed through the transformation of the oxyferic hydroxide into ferrous compounds which are more reactive under anaerobic conditions (Khalid *et al.*, 1977). It was also noted that percentage sorptions of P increases abruptly within the first few hours after the addition of the fertilizer. By the twelfth day the percentage of P sorption was 55.9 and 90.2 in the oxidised and reduced conditions respectively.

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