

## Short-Term Evolution of Phosphorus in an Ultisol

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### ABSTRACT

Evolution of residual phosphate was monitored as function of time on an Ultisol without cropping in a field trial at Sembawa Rubber Research Station, South Sumatra, Indonesia. Three treatments were imposed and either triple superphosphate at a rate of 600 kg ha<sup>-1</sup> containing 21.54% phosphorus (P) or lime at the rate of 4.14 tons ha<sup>-1</sup> was applied. During the 20 months of incubation, extractable phosphate as evaluated by hydrochloric acid-ammonium fluoride (Bray-I) declined in all treatments. The decrease in the P fertilized plot was more pronounced in relation to the control and the limed soil. Only 56% of P added to the soil was initially recovered as extractable P. This percentage was 30-40% in limed soils. No significant pH difference was recorded for all treated plots except for limed soils. An increase of 1.3 pH units was initially obtained by liming, but the pH dropped to about 0.9 unit after 20 months of incubation. In addition, total P in arable layer remained fairly constant. According to the

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recoveries of P added referring to 4.3 P 100 g<sup>-1</sup>, half-life of a single P dose was estimated at 31 months for a P fertilized soil and almost threefold delay for combination of P fertilization and lime application, which was obtained from the following equation:

$$\begin{aligned} \text{P fertilized: } \Delta P (\text{mg P } 100 \text{ g}^{-1}) &= 3.60 \text{ time (months)}^{-0.32} \\ \text{P fertilized + limed: } \Delta P (\text{mg P } 100 \text{ g}^{-1}) &= 2.49 \text{ time (months)}^{-0.21} \end{aligned}$$

## INTRODUCTION

Phosphorus (P) applied as fertilizer has the potential to supply P for plant roots through the increase of the labile or available P pool resulting in a subsequent increase in both the soil solution P and P exchanged between the solution and the solid phase that rapidly equilibrates with soil solution P (Morel et al., 1994; Morel et al., 1995). Due to the fact that P from fertilizer and native soil constituents will become gradually depleted from reactive fractions, which in non-calcareous soils are mainly present as sesquioxides.

Acidic tropical soils are mostly characterized by a poor fertilization history resulting in a low total P content with subsequent low available P. Additions of P in these soils are required to enhance and to sustain agricultural outputs (Friesen et al., 1997). Phosphate chemistry in acidic soils is complex, but is generally dominated by surface reactions with iron (Fe) and aluminum (Al) oxides, and kaolinite. The adsorbed phosphate, which will gradually become occluded in these compounds, will show a tendency of a concomitant decreasing solubility and unavailability for further plant use. As a practical consequence, the beneficial effect of P added as fertilizer to the soil will decrease irreversibly with time (Bramley and Barrow, 1992; Elisaba et al., 1992). Moreover, kinetics of these reactions seem to be significantly influenced by soil acidity (He and Zhu, 1997), rates of P supply (Ibrahim and Pratt, 1982), and lime (Bekele and Hofner, 1992). From a thermodynamic point of view, it is shown that the ultimate end products are variscite (AlPO<sub>4</sub>·2H<sub>2</sub>O) and strengite (FePO<sub>4</sub>·2H<sub>2</sub>O) which due to their low solubility are unable to supply sufficient P for plant growth. At pH ≤ 3.75 phosphate solubility generated by the variscite-gibbsite equilibrium is higher than that of strengite-goethite (Sofyan, 1995) which has shown practical consequences towards release P when the pH increases.

According to Larsen (1976), the evolution of applied P in a soil is involved in the following process: (1) depletion of the pool by cropping, (2) mobilization of native and residual P upon depletion from the P pool, and (3) immobilization of available P after enrichment of the P pool by application of soluble P fertilizer. Leaching of P under normal agricultural practices can be overlooked.

In this study, the third process of Larsen's sequence cited above will be investigated through following the fate of applied P fertilizer in an acidic soil which was incubated in field conditions without cropping.

## MATERIALS AND METHODS

The residual effect of a P fertilizer added in combination with lime to an Ultisol was evaluated in a field experiment without cropping at Sembawa Rubber Research Station, South Sumatra, Indonesia.

Dolomite was applied at the rate of 4.14 tons ha<sup>-1</sup> and P as triple superphosphate with an analytical P content of 21.54% at a rate of 600 kg ha<sup>-1</sup>. Phosphorus fertilizer and dolomite were applied as a powder to the soil surface with a 3x3 m<sup>2</sup> of each plot and thoroughly mixed with the depth. Weeds were removed by hand from the field and soils were left bare during the whole duration of the experiment. This lasted for 20 months and soil samples were taken up to a 20-cm depth every 4 months and were sampled regularly on March 26, July 24, November 21, 1996 and March 25, July 18, 1997.

To characterize the general soil chemical status, soil pH was determined in water at 1:5 ratio and in 1 N KCl at 1:2.5 ratio (Cottenie et al., 1982). Soil P availability was extracted using Bray-I method in a 0.03 N NH<sub>4</sub>F + 0.025 N HCl and P total was digested in 18% HClO<sub>4</sub>. The fractionation of Al-P and Fe-P forms were determined in 0.1 N NaOH + 1 M NaCl + 0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> + 1 M NaHCO<sub>3</sub>, while Ca-P was extracted with 1 N HCl and Fe(hydr)oxide-P with 0.3 M Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> + 1 M NaHCO<sub>3</sub> + 1 g Na<sub>2</sub>S<sub>2</sub>O<sub>4</sub> (Olsen and Sommers, 1982). All P was determined in Scheel solution. The N total in soil was recovered using the Kjeldahl procedure (Bremner and Mulvaney, 1982) and total C-organic was determined using the Walkley-Black method (Nelson and Sommers, 1982). Exchangeable Ca, Mg, and K were recovered in 1 N NH<sub>4</sub>OAc at pH 7 (Thomas, 1982) and exchangeable Al was determined in 1 N KCl (Barnhisel and Bertsch, 1982). Effective cation exchange capacity (ECEC) was calculated as the sum of basic cations in addition to exchangeable Al. Aluminum saturation was calculated as the ratio of exchangeable Al divided by the ECEC. All soil samples were analyzed for pH, total P, and extractable P. The general soil chemical characterization is presented in Table 1.

## RESULTS

### Soil Characterization

From Table 1, it is apparent that the soil was characterized by a relatively low effective ECEC and high exchangeable Al with 82% Al saturation. The pH (H<sub>2</sub>O) of the soil was 4.72, and the soil also showed a low content of exchangeable basic cations. The pH (KCl) of the Ultisol studied was below the pH (H<sub>2</sub>O), indicating that a net negative charge was present on clay surfaces (Mekaru and Uehara, 1972). Phosphorus recovery according to the Bray-I method was clearly below the critical level, which was assumed to be at 2 mg per 100 g soil (Olsen and Sommers, 1982). Most P was present as Al and Fe forms. In addition, a relatively low amount of total organic carbon and N in this uncultivated Ultisol was also observe.

TABLE 1. Chemical properties of sod studied.

Soil analyses	Value
pH (H <sub>2</sub> O)	4.72
pH (KCl)	3.73
P-Bray-I (mg P 100 g <sup>-1</sup> )	1.33
P-total (mg P 100 g <sup>-1</sup> )	18.47
Al-P and Fe-P (mg P 100 g <sup>-1</sup> )	10.11
Ca-P (mg P 100 g <sup>-1</sup> )	5.20
Occluded P (mg P 100 g <sup>-1</sup> )	0.73
C-organic (%)	1.47
N-total (%)	0.13
Ca [Cmol(+) kg <sup>-1</sup> ]	0.28
K [Cmol(+) kg <sup>-1</sup> ]	0.15
Na [Cmol(+) kg <sup>-1</sup> ]	0.09
Mg [Cmol(+) kg <sup>-1</sup> ]	0.10
ECEC [Cmol(+) kg <sup>-1</sup> ]	3.65
Al-exch. [Cmol(+) kg <sup>-1</sup> ]	3.03
Al-saturation (%)	82

Total P content of the soil studied was very low amounting to 18.47 mg P 100 g<sup>-1</sup>. This is due to the poor phosphate fertilization history of the area sampled. Fuad (1976) confirmed to this total P content by stating that Ultisols derived from humid tropical conditions had a distinctly lower amount of total P ranging from 20-30 mg P 100 g<sup>-1</sup>. Kalpage and Wong (1978) found that sequence of total P content was Oxisols>Entisols>Inceptisols>Ultisols.

### Soft pH

The pH (H<sub>2</sub>O) values showing the mean of three replications are presented in Table 2. No significant pH differences appeared between the control and the P fertilized soil, the pH range for the control varied from 4.40 to 4.55. Comparable results ranging from 4.44 to 4.56 were obtained for the P fertilized plot.

At the rate of 4.14 tons lime ha<sup>-1</sup>, the pH initially increased by 1.3 units versus the control and then dropped to a difference of 0.9 units after 20 months. The pH increase was 1.2 and 0.7 units, respectively, when a combination of lime and P fertilizer was added. To that respect, pH values of treated soils significantly decreased linearly over the period monitored (P<0.05) with the equations:

$$\begin{array}{ll}
 \text{pH control} = 4.49 - 0.003 \text{ time (month)} & r = 0.24^{\text{ns}} \\
 \text{pH fertilized soil} = 4.52 - 0.004 \text{ time (month)} & r = 0.44^{\text{ns}} \\
 \text{pH limed soil} = 5.89 - 0.03 \text{ time (month)} & r = 0.89^* \\
 \text{pH limed+fertilized} = 5.85 - 0.04 \text{ (month)} & r = 0.97^{**}
 \end{array}$$

TABLE 2. Values of observed pH (H<sub>2</sub>O) as function of the incubation time.

Incubation time (months)	Control	P fertilized	Limed	P fertilized and limed
4	4.55±0.01	4.56±0.01	5.86±0.26	5.76±0.21
8	4.42±0.01	4.52±0.06	5.56±0.01	5.53±0.05
12	4.40±0.14	4.47±0.17	5.37±0.01	5.36±0.03
16	4.50±0.10	4.49±0.14	5.27±0.27	5.23±0.10
29	4.45±0.01	4.44±0.01	5.32±0.16	5.18±0.03

When these linear equations are maintained, it is expected that after 4 years the effect of a single lime dose on pH will be annihilated in this highly weathered tropical soil.

#### Total Phosphorus

Total P contents (mg P 100 g<sup>-1</sup>) of the 4 plots as a function of sampling time (month) are presented in Table 3, for the control and the limed plot, average values amounting to, respectively, 18.06±0.24 and 18.20±0.23 mg P 100 g<sup>-1</sup> were obtained. Additionally, for the P fertilized soils either in the absence or presence of lime, mean values of total P, respectively, 22.78±0.41 and 22.98±0.42 mg P 100 g<sup>-1</sup> were recorded. It was obvious that these two sets led to similar results.

Assuming that 3×10<sup>6</sup> kg of soil was equivalent to 1 ha, application of a P fertilizer dose of 600 kg TSP per ha at a content of 21-54% P, was estimated to be 4.3 mg P 100 g<sup>-1</sup>. This value is in close agreement with the net experiment difference of total P content between P fertilized plot and the control on the one hand and both limed plots on the other, respectively 4.72 and 4.78 mg P 100 g<sup>-1</sup>, were recovered. Because no substantial P loss was observed during the whole duration of the experiment, it can be concluded that P will fully remain in the arable layer and that no significant leaching out of the arable layer will occur. This statement fully underscribes many earlier observations that under normal agricultural practices, P remained essentially immobile in the arable layer (Vanderdeelen, 1995; Sofyan, 1995).

#### Extractable Phosphorus

The combination of hydrochloric acid and ammonium fluoride is expected to extract easily acid soluble P, mainly highly or weakly soluble calcium phosphate, and loosely bound phosphate which is onto sesquioxides as well as the amorphous precipitates containing P (Olsen and Sommers, 1982). This extraction method, known as Bray-I, is a generally adopted method to evaluate the P status of acidic soils in Indonesia.

TABLE 3. Total P content (mg P 100 g<sup>-1</sup>) for the soils.

Incubation time (months)	Control	P fertilized	Limed	P fertilized and limed
4	18.42	22.97	19.75	23.50
8	17.67	22.78	17.75	23.33
12	18.06	23.00	18.25	23.00
16	18.16	23.16	18.23	22.75
20	18.00	22.00	18.00	22.33
Mean±std	18.06±0.24	22.78±0.41	18.20±0.33	22.98±0.42

Analytical extractable P data showing the mean of three replications for the 4 treatments as a function of sampling time are presented in Table 4. During the 20 months of incubation, a linear decrease of extractable P was obtained ranging significantly from 1.73 to 1.47 for the control, and from 1.43 to 1.03 mg P 100 g<sup>-1</sup> for the limed soil with the following two linear equations:

$$\text{Extractable P (mg P 100 g}^{-1}\text{) for control} = 1.82 - 0.017 \text{ time (month)} \quad r = -0.97^{**}$$

$$\text{Extractable P (mg P 100 g}^{-1}\text{) for limed soil} = 1.52 - 0.24 \text{ time (months)} \quad r = -0.99^{**}$$

A similar behavior, but nonlinear decrease was observed in P fertilized plots showing a significant decrease from 4.15 to 2.90 mg P 100 g<sup>-1</sup>, and from 3.32 to 2.36 mg P 100 g<sup>-1</sup> for the combined P fertilizer and lime treatment with the power equations:

$$\text{Extractable P (mg P 100 g}^{-1}\text{) for fertilized soil} = 5.55 \text{ time (month)}^{-0.22} \quad r = 0.99^{**}$$

$$\text{Extractable P (mg P 100 g}^{-1}\text{) for fertilized+limed} = 4.41 \text{ time (month)}^{-0.20} \quad r = 0.99^{**}$$

These results confirmed the general trend as shown by Sofyan (1995) that with time of incubation a decrease of extractable P in the soil was recorded due to irreversibility adsorption of P on Al- and Fe-(hydr)oxides. The decline with time of extractable P in the fertilized plots was markedly more pronounced than in limed soils as shown in Figure 1.

It was also clear that the decrease of extractable P for the two P fertilized plots was occurring much faster during the first eight months than from the 8th up to the 20th month. This approach was also strongly supported by Barrow (1980) in order to describe the effectiveness of fertilizers in soils. It is due to the fact that the reaction of soil and P in the soil solution took place in two steps, which were a rapid superficial adsorption reaction onto soil particles, and a slower step in which the phosphate was converted into a more firmly held form using occlusion and/or diffusion into matrix. This supported the hypothesis that the amount of extractable P in acidic soils will continue to decrease with time until the P level in the originally unfertilized soil is reached (Ryan et al., 1985; Freese et al., 1992; He and Zhu, 1997). Because of the poor P fertilization history in this Ultisol, it is foreseen that the

TABLE 4. Extractable P (mg 100 g<sup>-1</sup>) as function of aging time.

Incubation time (months)	Control	P fertilized	Limed	P fertilized and limed
2	1.73±0.07	4.15±0.10	1.43±0.15	3.32±0.03
8	1.70±0.05	3.46±0.03	1.32±0.22	2.88±0.09
12	1.66±0.07	3.17±0.20	1.23±0.10	2.73±0.22
16	1.53±0.16	3.06±0.10	1.15±0.19	2.55±0.44
20	1.47±0.01	2.90±0.02	1.03±0.02	2.36±0.10

extent of the potential phosphate adsorption sites will essentially remain unoccupied. In addition, the study of the first authors showed that besides aging time, the amount and morphology of sesquioxides also played an important role in the transformation of soluble P to less soluble phosphate forms.

## DISCUSSION

### Phosphorus Recovery

Data displayed in Table 5 showed the recoveries of extractable P as obtained in P amended soils. These recoveries were calculated by subtraction of the extractable P obtained in the P fertilized soil to the control and in combination of P fertilizer and lime to the limed plot on the other hand.

With reference to the P added at 4.3 mg 100 g<sup>-1</sup>, the recovery of extractable P amounting to 2.42 mg 100 g<sup>-1</sup> after 4 months was obtained which only represented 56%; this percentage dropped to 33% after 20 months. Much lower values were obtained when lime was present, the initial value of 44% decreased to almost 31%. On a qualitative scale, it is expected that due to immobilization phenomena of the P added to this Ultisol, part of the latter will be involved in occlusion reactions making the P neither available for crops nor for chemical extraction.

### Phosphorus Evolution as Function of Aging Time

Within the 20 months monitored, total P remained fairly constant for all treatments, but extractable P significantly decreased with time. Application of P fertilizer in soluble form resulted in an initial fast decrease of extractable P as illustrated in Figure 2; a constant decrease of extractable P was obtained for the control and limed soil. The extractable P content was significantly affected by lime application because addition of lime declined the initial P by about 15 to 20%.

As referenced by the values of the correlation coefficient for P fertilized soils, a power equation seemed to fit smoothly the P evolution as function of aging time;

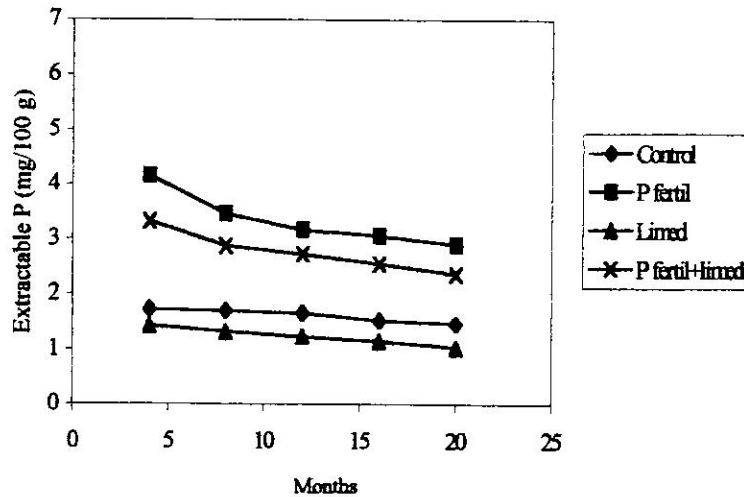


FIGURE 1. Evaluation of Bray-I extractable P ( $\text{mg P } 100 \text{ g}^{-1}$ ) as function of aging time.

an initial fast decrease as monitored by extractable P using Bray-I method seemed to slow with time. Larsen et al. (1976) first introduced the concept of half-life of P added, in order to quantify the P immobilization rate. The concept referred to the time required to reduce the initial P amount added to its half. When a suitable P extractant agent is used, displaying closely the evolution of plant available P as function of time, the rate of P immobilization in the soil can be discovered. In this study, the half-life of the P fertilized soil was estimated from the data of extractable P. Difference of extractable P between fertilized soils and the control are called  $\Delta P$  and are presented in Table 6. The values were recovered by subtraction of calculated P from the control and limed plot concerned to the P contents extracted from the P fertilized and the lime P fertilized plot. Using these net values in Table 6, as displayed in Figure 2, the following power equations are obtained:

$$\text{For P fertilized plot: } \Delta P (\text{mg } 100 \text{ g}^{-1}) = 3.60 \text{ time (months)}^{-0.32} \quad r = -0.98^{**}$$

$$\text{For P fertilized+lime plot: } \Delta P (\text{mg } 100 \text{ g}^{-1}) = 2.49 \text{ time (months)}^{-0.21} \quad r = -0.99^{**}$$

Based on these power equations, half-life of added P as monitored by the Bray-I method and referenced to the first net P difference which was obtained after 4 months were computed. Half-life of added P in absence of lime amounted to 31 months. In the presence of lime, P half-life seemed to undergo unfold retardation versus the previous case. These results met to a large extent the conclusion as derived from solubility calculations of phosphate compounds (Sofyan, 1995).



TABLE 5. Phosphorus recovery (mg P 100 g<sup>-1</sup>).

Incubation time (months)	P recovery			
	As extractable P			
	In P fertilized plot		In P fertilized+limed plot	
	mg P 100 g <sup>-1</sup>	%	mg P 100 g <sup>-1</sup>	%
4	2.42	56	1.89	44
8	1.76	41	1.56	36
12	1.51	35	1.50	35
16	1.53	36	1.40	32
20	1.43	33	1.33	31

Comparing solubility of Fe-P and Al-P, a net increase was observed when pH increases. However, at pH 5.5-6.0, these P solubility curves intersect with the pH and Ca-P solubility, resulting in a P release from Fe and Al compounds in favor of calcium phosphates or mixed Fe-Al-Ca phosphates, while show probably a higher solubility and availability than pure Al-P and/or Fe-P (Lindsay, 1979).

It is clear that more work in the period from 0 to 4 months should be done in order to know the process involved with the very fast P decrease in this soil. In effect, from 4.3 mg P 100 g<sup>-1</sup> soil added at the start of this experiment, respectively 2.4 in

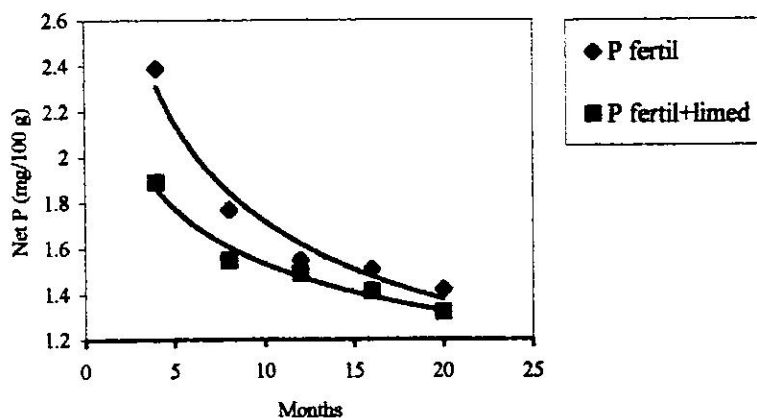


FIGURE 2. Relationship between net P recoveries according to Bray-I and incubation time.

TABLE 6. Net P differences in extractable P (mg P 100 g<sup>-1</sup>) of the P treated plot.

Incubation time (months)	In P fertilized plot	In P fertilized+limed plot
4	2.39	1.89
8	1.77	1.55
12	1.55	1.49
16	1.51	1.41
20	1.42	1.32

the absence and 1.9 mg P 100 g<sup>-1</sup> in the presence of lime were recorded after 4 months. In these conditions and due to the power fit equation, the values of the half-life obtained will be clearly overestimated. With reference to the semi-field experiments, Sofyan (1995) obtained P half-life for Belgium acidic soils ranging from 3 up to 19 years.

To what extent specific soil properties and poor phosphate fertilization history of this soil will be inherently linked to this very essential phenomenon in tropical soils is difficult to assess. Moreover, we cannot expect that half-life of applied P fertilizer should be independent of the methodology applied in order to recover the available phosphate.

### CONCLUSIONS

An almost constant pH of the control and P fertilized plots was recorded during the 20 months monitored. An increase of 1.3 pH units was initially obtained by liming at a rate of 4.14 tons ha<sup>-1</sup>. After 20 months, the pH difference dropped to about 0.9 units. Total P content of this Ultisol after application of P fertilizer either in the absence or presence of lime remained fairly constant. Almost all P added was recovered as total P. With aging time, the extractable P decreased in function of time. The decline of extractable P in fertilized plots was more pronounced. Only 56% of P added to the soil was recorded as initially extractable P. This percentage dropped to 30-40% in limed soils. According to the P recoveries as monitored using the Bray-I method, and referred to the first soil sampling, half-life of added P at a rate of 600 kg TSP ha<sup>-1</sup> was obtained ranging from 31 months for the fertilized plot in absence of lime and to almost threefold delay when a combination of P with lime was applied.

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