



## Effect of byproduct, nitrogen fertilizer, and zeolite on phosphate rock dissolution and extractable phosphorus in acid soil

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### Abstract

Coal combustion by products (BP) and phosphate rock (PR) have been widely used as cost-effective amendments for acid soils. Information is needed on the proper combination of BP with chemical fertilizers or other organic and inorganic amendments to improve the productivity of acid soils. Chemical analysis and soil incubation studies were carried out to examine the effect of BP, N fertilizers, and zeolite on dissolution of PR and on the status of extractable P in acid soil. Several kinetic models were compared for describing PR dissolution in acid soils that received different amounts of BP, different forms of N fertilizer, and zeolite. PR dissolution in acid soil measured by 0.5 M NaOH extraction was best described by a Langmuir kinetic model ( $r^2=0.988^{**}$ ), followed by an Elovich ( $r^2=0.950^{**}$ ), a two-constant rate ( $r^2=0.947^{**}$ ), a parabolic diffusion ( $r^2=0.905^{**}$ ), and a first-order reaction equation ( $r^2=0.637^*$ ). A second-order reaction equation was the poorest among various models tested ( $r^2=0.484$ ). Addition of BP, N fertilizers, and zeolite to the PR-amended soil did not affect the good fitness of PR dissolution to these kinetic equations. Increasing BP addition decreased initial and average dissolution rate and potential maximum dissolution of PR during the incubation period of 132 days as calculated from the Elovich and Langmuir kinetic models. In general,  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$  increased the initial rate and decreased slightly the average PR dissolution rate due to a rapid but short-term acidifying effect. On the other hand, urea and zeolite decreased the initial rate of PR dissolution due to higher pH and increased the average PR dissolution rate because of long and persistent acidification by urea and slow but continued removal of Ca by zeolite. The effect of N fertilizers and zeolite on the potential maximum dissolution of PR was related to amounts of BP added. Extractable P in the PR-amended soils as determined by 0.5 M  $\text{NaHCO}_3$  was closely correlated with P released by PR dissolution. The ratio of increased  $\text{NaHCO}_3$ -extractable P due to PR application divided by the total amount of P released from PR dissolution measured by NaOH extraction might reflect relative availability of P from PR dissolution. This ratio was increased by addition of BP, urea, and zeolite but decreased by  $\text{NH}_4\text{NO}_3$  and  $(\text{NH}_4)_2\text{SO}_4$ .

### Introduction

There has been increasing environmental concern on the increased loading of P into surface waters from agriculture (Carpenter et al., 1998). More research is needed to understand the balance between applying P

for maximum economic crop yield and decreasing P movement to surface waters from farm land in order to minimize the risk of eutrophication. In relation to this last point, phosphate rock may have advantage over easily soluble P fertilizers since it dissolves slowly in soil and leads to lower potential for eutrophication of surface waters. Phosphate rock has proved to be an agronomically effective low cost P fertilizer for highly

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weathered acid soils, as it provides both P and Ca, which are frequently deficient in these soils. Phosphate rock appears to be a good source of P because of its high dissolution rate in acid soils (He et al., 1996a,b; Wright et al., 1992).

Coal combustion byproduct gypsum, a solid waste from power plants, has recently been considered as a potential amendment to reduce Al toxicity and improve growth and nutrition of plants in acid soils (Clark et al., 1994) because of its ability to partially replace exchangeable Al from the soil with Ca. However, it was found in our earlier studies that BP considerably decreased PR dissolution in soil when both were applied together (He et al., 1996a). The dissolution rate of PR may be too slow to meet the demand of annual crops for P supply in the BP-amended soil, which may discourage the acceptability of PR mixed with BP as a fertilizer amendment for acid soil. The major factors affecting PR dissolution in acid soils are the availability of  $H^+$ , moisture, and removal of Ca and P from the solution (He et al., 1996b). Highly weathered acid soils are suitable for the direct application of PR as they provide  $H^+$ , have low concentrations of Ca and P in solution, and have a high P fixation capacity. But the cation exchange capacity (CEC) of acid soils is usually low, and the Ca concentration of soil solution around the PR particles builds up rapidly, thus slowing the dissolution rate of the PR in soil.

Application of N fertilizers is essential for good crop yields, particularly in acid soil where organic matter is low. Nitrogen fertilizers in the  $NH_4^+$  form have long been recognized as increasing soil acidity (Tisdale and Nelson, 1975) due to release of  $H^+$  with plant absorption of  $NH_4^+$  and with nitrification of  $NH_4^+$ . Theoretically, soil acidification from N fertilization can be used to counteract the liming effect of BP and enhance PR dissolution in BP- and/or lime-amended soils. In addition, acid soils usually lack appropriate levels of N to support plant growth and application of N fertilizer is a common practice for sustainable crop production in the acid soil regions. An understanding of the interactions among BP, PR, microorganisms, and N fertilizers will be useful for the management of N fertilization. Addition of  $(NH_4)_2SO_4$  and urea along with PR to acid soil has been observed to increase PR dissolution and P uptake by plants (Chien, 1979; Jones, 1948). But little information is available as to chemical interactions of N fertilizers with PR and the subsequent effect on P availability in acid soils.

Zeolite has long been recognized as an exchanger of cations and anions and is often used for increasing CEC and removing some heavy metals from contaminated soils (Chlopecka and Adriano, personal communication). Addition of  $NH_4^+$ -saturated zeolite was shown to increase PR dissolution due to removal of  $Ca^{2+}$  by zeolite through cation exchange (Allen et al., 1993). Zeolite may be useful in BP-amended soil to enhance PR dissolution.

Phosphate rock, inorganic fertilizers (NPK), and BP may be applied in combination rather than alone in order to increase crop yields in acid soils. Previous work indicated that application of limestone and BP decreased both PR dissolution and available P from PR in soil (He et al., 1996a,b), but increased P availability efficiency (the amount of plant yield produced (mg) per unit of extractable P (mg)) and P utilization efficiency (the amount of plant yield produced (mg) per unit of P in the plant (mg)) of soil P by plants due to improved development of the plant roots (Baligar et al., 1997; He et al., 1997a, b). In addition, BP might also increase the availability of P from PR dissolution by reducing P adsorption by variable-charge minerals through P-Ca association. Further information is needed to understand crucial chemical interactions among PR dissolution and BP, N fertilizers, and zeolite.

Attempts have been made to adjust the time and amount of PR application so that P released could meet the plant P demand for growth (Mackay et al., 1986; Sikora & Giodano, 1995; Wright et al., 1991, 1992). It is essential to predict PR dissolution in soils as affected by soil properties in order to time its application for P availability. Chien et al. (1980) compared several kinetic models for describing PR dissolution in soils and concluded that an Elovich equation gave the best fit. He et al. (1996a) applied a first-order, an Elovich-type and a Langmuir-type kinetic equation to quantitatively assess the effect of BP, limestone, and cellulose on the dissolution of PR in soils. Some parameters including the initial (*A*) and average dissolution rate constant (*b*) from the Elovich equation, and the potential maximum dissolution of PR (PMDPR) from the Langmuir equation were useful for predicting PR dissolution as affected by soil amendments.

The purpose of this research was to elucidate the effect of BP, different N fertilizers, and zeolite applied alone or in combination on PR dissolution. A further aim of this research was to examine the effect of these amendments on the amount of Olsen P released from PR. Several commonly used kinetic models were com-

pared and the best-fit models were used to describe the effects of the above amendments on the rate of PR dissolution in acid soil.

### Materials and methods

An acidic Lily loam (Typic Hapludult, sand 510 g kg<sup>-1</sup>, silt 380 g kg<sup>-1</sup>, and clay 110 g kg<sup>-1</sup>) was collected from the 0- to 50-cm depth (of a layer with similar soil materials), mixed, passed through a 2.0-mm sieve, and stored below 4°C in preparation for the research. A subsample was air-dried for chemical analysis. Selected properties of the soil were: 12.6 g kg<sup>-1</sup> organic C content measured with a dry combustion analyzer (model CHN-600, LECO Corporation, St. Joseph, MI, USA<sup>1</sup>), 4.5 pH (H<sub>2</sub>O), 3.9 pH (0.01 M CaCl<sub>2</sub>), 2.98 mg Bray P<sub>1</sub> extractable P kg<sup>-1</sup> soil, 0.42 mg NaHCO<sub>3</sub> extractable P kg<sup>-1</sup> soil (Olsen and Sommers, 1982), and 0.74 cmol<sub>c</sub> kg<sup>-1</sup> 1.0 M NH<sub>4</sub>OAc exchangeable (Ca+Mg) (Thomas, 1982). A highly carbonate-substituted PR (North Carolina PR) containing 132 g P and 338 g Ca kg<sup>-1</sup> was obtained from Texasgulf, Inc., and passed through a 150-μm sieve prior to use. The BP was a wallboard-quality gypsum (BP-#16 from the Beckley ARS collection), produced by an in situ forced oxidation limestone-based scrubber (Clark et al., 1994). The BP contained up to 900 g kg<sup>-1</sup> CaSO<sub>4</sub>, with 220 g kg<sup>-1</sup> Ca, 185 g kg<sup>-1</sup> S, <500 mg total P kg<sup>-1</sup>, and no detectable amounts of 0.5 M NaOH-, Bray P<sub>1</sub>-, or Olsen P-extractable P. The zeolite used was from natural source (clinoptilolite) with Na as the dominant cation (pH 9 and 40 g kg<sup>-1</sup> CCE-calcium carbonate equivalent).

### Incubation study

The experiment was designed as 5 × 2 × 3 factorial arrangements of 30 treatments, including five basic treatments: the control (without amendment), NH<sub>4</sub>NO<sub>3</sub> (AN), (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (AS) or urea (U) at 200 mg N kg<sup>-1</sup>, and zeolite at 10 g kg<sup>-1</sup>; two PR amounts (0 and 392 mg P kg<sup>-1</sup>), and three BP amounts (0, 10, 25 g kg<sup>-1</sup>). There were three replications for each treatment. Portions of fresh soil were weighed and thoroughly mixed with amendments. The total weight of each soil-amendment mixture was 1.0 kg (oven-dry

basis). The moisture content of the mixture was adjusted to 230 g kg<sup>-1</sup> (w/w). The mixtures were placed in 3-l plastic containers (12.3 × 12.5 × 19.2 cm) and incubated in a temperature-controlled chamber at 23°C. Each container was covered with parafilm to prevent moisture loss while allowing for air exchange during incubation. Subsamples of 1.0 g soil (oven-dry basis) in duplication were taken for measurements of PR dissolution, labile P, and pH at intervals of 0 (sampled immediately after being prepared), 7, 14, 21, 35, 56, 77, and 132 days of incubation. Exchangeable Ca, and Mg were measured at the end of incubation (132 days).

### Chemical Analyses

#### PR dissolution

PR dissolution was measured by a modified 0.5 M NaOH extraction method (He et al., 1996a). Briefly, 1.0 g soil (oven-dry basis) was equilibrated on a mechanical shaker with 50 ml of 0.5 M NaOH solution for 16 h. Extractable P was determined by extracting 1.5 g of subsoil sample with 30 ml of 0.5 M NaHCO<sub>3</sub> (pH 8.5) for 0.5 h. This extractant was used because the extractable P by this method was best related to other tests and plant P uptake (He et al., 1997a,b). Phosphorus concentration in the supernatant was determined after filtration through Whatman No. 42 filter paper (Whatman Int. Ltd, Springfield Mill, Maidstone, Kent UK). Phosphorus in both the NaOH and NaHCO<sub>3</sub> extracts was determined colorimetrically by an ascorbic acid-phosphomolybdate method (Olsen and Sommers, 1982). A light coloration of dissolved organic matter in the NaOH extracts did not interfere with the P determination at 882 nm wavelength because a high solution/soil ratio (50:1) was used during extraction (He et al., 1996a). The difference in P level (ΔP) between the PR-treated and the control samples was used as an estimate of PR dissolution. Exchangeable Ca<sup>2+</sup> and Mg<sup>2+</sup> were extracted with 1.0 M NH<sub>4</sub>Ac, and determined by inductively coupled-plasma spectrophotometry (Simultaneous ICP, Model JY 46P, Lorgumeace Cedex, France). Soil pH was determined with an Orion pH meter (model 520 A) at 1:1 soil/water ratio (w/v).

#### Kinetic description

Six kinetic models were compared for describing PR dissolution in soil: (1) a first-order reaction ( $\ln C_t = \ln C_o + kt$ , where  $C_o$  is the PR dissolution at zero time and  $C_t$  is the PR dissolution at time  $t$  and  $k$  is the rate

\* Mention of particular companies or commercial products does not imply recommendations or endorsement by the Virginia Polytechnic Institute and State University, Blacksburg, VA or the USDA over other companies or products not mentioned.

constant); (2) a second-order reaction ( $1/C_t = 1/C_o + kt$ , the definition of  $C_t$ ,  $C_o$ ,  $k$ , and  $t$  are the same as the first-order equation); (3) a parabolic diffusion ( $C_t = C_o + kt^{1/2}$ , the definition of  $C_t$ ,  $C_o$ ,  $k$ , and  $t$  are the same as the first-order equation); a two-constant rate ( $\ln C_t = \ln k + (1/m) \ln t$ , where  $k$  and  $m$  are the constants with  $k$  having different physical meaning from the first-order reaction); (5) a Langmuir-type kinetic ( $t/C_t = a + bt$ , with  $a = 1/kq_m$ , and  $b = 1/q_m$ ,  $k$ , the constant,  $q_m$ , defined as PMDPR in this study); and (6) an Elovich-type kinetic equation ( $c_t = a + b \ln t$ , with  $a = C_o - (1/\beta) \ln(\alpha\beta)$ , and  $b = 1/\beta$ , where  $\alpha$  and  $\beta$ , the constants). The initial ( $A$ ) and average dissolution rate ( $b$ ) from the Elovich equation, and the potential maximum dissolution of PR from the Langmuir equation, were used to quantitatively assess the effect of BP, fertilizers and zeolite on the dissolution of PR. A more detailed derivation of the Elovich-Langmuir-type kinetic equation were given by He et al. (1996a).

### Statistical Analyses

A simple regression procedure (SAS Institute, 1989–1996) was applied to test the fitness of the PR dissolution data to the three kinetic models. A general linear model procedure (SAS Institute, 1989–1996) was used to determine the significance of main effects (three levels of coal combustion byproduct and nitrogen fertilizers, and zeolite) and interactions on soil pH, phosphate rock dissolution (PR-P) in soil, 0.5 M NaHCO<sub>3</sub> extractable P (Olsen-P), and the Olsen-P/PR-P ratio.

## Results and discussion

### General characterization

The PR had an initial rapid dissolution, which was completed in 30 days, followed by a slow and steady dissolution stage that persisted more than 100 days (Fig. 1a–c). Addition of AN or AS enhanced PR dissolution, especially in the first stage of dissolution, whereas PR dissolution at the first stage was lower but increased at the second dissolution stage with urea or zeolite (Fig. 1a). The different effects on PR dissolution between NH<sub>4</sub> salts and urea was related to a rapid short time acidification by the former and an increased pH during the first few weeks due to hydrolysis of urea followed by a long term slow pH decrease from nitrification of the released NH<sub>4</sub> (Fig. 2a, b). The AS that theoretically produces more H<sup>+</sup> through nitrification

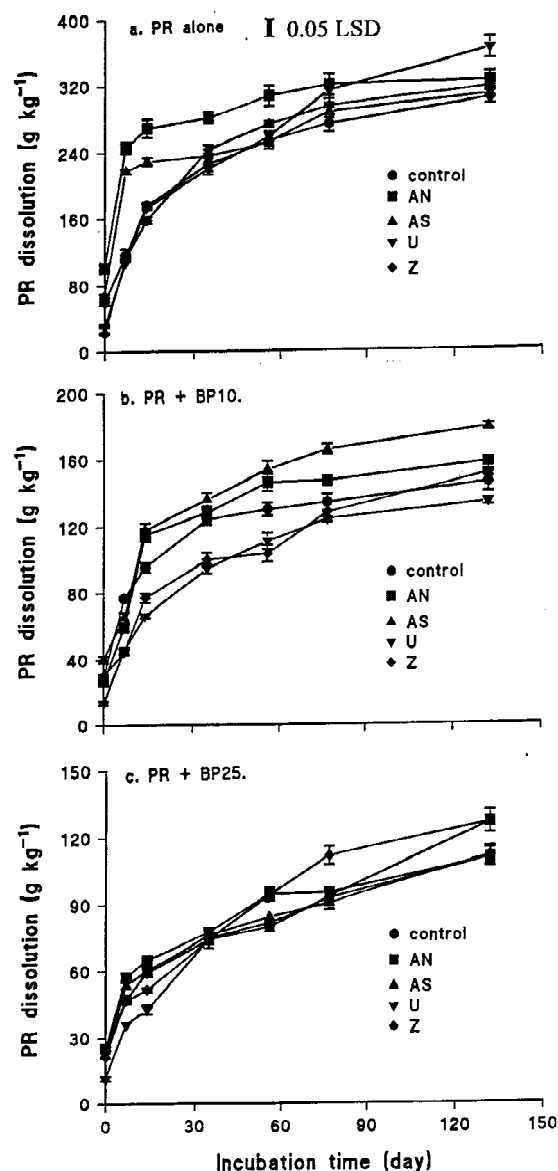


Figure 1. Effect of ammonium nitrate (AN), ammonium sulfate (AS), urea (U), and zeolite (Z) on phosphate rock (PR) dissolution in an acidic soil: (a) PR at 392 mg P kg<sup>-1</sup>, (b) PR + BP10 (at 10 g kg<sup>-1</sup>) and (c) PR + BP25 (25 g kg<sup>-1</sup>).

of NH<sub>4</sub><sup>+</sup> than the AN had less net acidifying effect than the later (Fig. 2a), probably due to release of surface OH<sup>-</sup> by SO<sub>4</sub><sup>2-</sup> through ligand exchange (He et al., 1997). The effect of zeolite was associated with neutralization of soil acidity due to its high pH (pH 9 with Na as dominant adsorbed cation) as shown in Fig. 2a, b, and persistent removal of Ca from soil solution through exchange with Na (Allen et al., 1993).

Table 1. Average coefficient of simple determination ( $r^2$ ) of various kinetic models for dissolution of phosphate rock in acid soil ( $n=30$ )

Models	Equation	$r^2$
First-order reaction	$C_t = \ln C_o + kt$	0.637*
Second-order reaction	$1/C_t = 1/C_o + kt$	0.484
Parabolic diffusion	$C_t = C_o + kt^{1/2}$	0.905**
Two-constant rate equation)	$\ln/C_t = \ln k + (1/m) \ln t$	0.947**
Langmuir-type equation	$t/C_t = a + bt$	0.988**
Elovich-type equation	$C_t = a + blnt$	0.950**

\*, \*\*Significance at 0.05 and 0.01 probability level, respectively.

Addition of BP decreased soil pH (Fig. 2c–f), due to replacement of surface H by added Ca (Baligar et al., 1997). However, by comparing Fig. 1b with Fig. 1a it can be seen that addition of BP at 10 g kg<sup>-1</sup> reduced PR dissolution almost by half, but did not change the two-stage dissolution characteristics of the PR in acid soil. Similar results were obtained with other source of BP (He et al., 1996a). The negative effect of BP on PR dissolution was mainly related to its high Ca content (He et al., 1996b). Addition of AN and AS partially countered this effect, but urea or zeolite addition further decreased the PR dissolution in the BP amended soil although this effect became less evident at later incubation stages (Fig. 1 b). Phosphate rock dissolution decreased with increasing BP addition, and at the higher BP amount (25 g kg<sup>-1</sup>) AN slightly increased PR dissolution in 30 days, AS showed little effect, whereas urea and zeolite negatively affected PR dissolution at an early stage but slightly increased PR dissolution at the later stage during incubation (Fig. 1c). These results indicate that Ca plays a dominant role in PR dissolution and the acidifying effect of nitrogen fertilizer on PR dissolution becomes less important in the BP-amended soil compared to soil without BP.

#### Kinetics of PR dissolution

Several kinetic models were compared for describing PR dissolution in acid soils that received different amounts of BP, different forms of nitrogen fertilizer, and zeolite. Phosphate rock dissolution in the acid soil measured by 0.5 M NaOH extraction was best described by a Langmuir kinetic model ( $r^2=0.988$ \*\*), followed by an Elovich ( $r^2=0.950$ \*\*), a two-constant rate ( $r^2=0.947$ \*\*), a parabolic diffusion ( $r^2=0.905$ \*\*), and a first-order reaction equation ( $r^2=0.637$ \*). A second-order reaction equation was the poorest based

Table 2. The effects of soil amendments on initial ( $A$  value) and average rate ( $b$  value) obtained from Elovich and potential maximum dissolution of PR (PMDPR) from Langmuir-type kinetic equation in acid soil

Treatments <sup>a</sup>	$A$ value (g kg <sup>-1</sup> PR day <sup>-1</sup> )	$b$ value (g kg <sup>-1</sup> PR day <sup>-1</sup> )	PMDPR (g kg <sup>-1</sup> PR)
Without BP			
Control	44.5c	50.8b	297c <sup>b</sup>
AN	122.8a	47.9b	327b
AS	92.2b	44.7c	289c
U	-4.6e	65.7a	351ab
Z	6.0d	64.9a	353a
With BP at 10g kg <sup>-1</sup>			
BP10	29.5a	25.0b	143b
BP10+AN	21.4b	30.0a	163a
BP10+AS	32.1a	28.9a	170a
BP10+U	7.2c	24.3b	132b
BP10+Z	19.6b	22.1c	135b
With BP at 25 g kg <sup>-1</sup>			
BP25	21.2b	15.2c	96b
BP25+AN	26.2a	15.0c	93b
BP25+AS	21.6b	15.6bc	95b
BP25+U	4.6d	18.9a	106a
BP25+Z	16.2c	17.2ab	103ab
Significance			
Main factor (BP rate)	***	***	***
Subfactor (control, AN, AS, U, and Z)	***	***	***
Main factor × subfactor	***	***	***

<sup>a</sup>PR, Phosphate rock; BP, coal combustion byproduct; AN, ammonium nitrate; AS, ammonium sulfate; U, urea; Z, zeolite; and 10 and 25 indicate application rate at 10 and 25 g kg<sup>-1</sup>, respectively. <sup>b</sup>Different letters after means indicate significance at 0.05 probability level for different treatments within the same BP level. \*\*\*Significance at 0.001 probability level.

on the fit to the experimental data among the models tested ( $r^2=0.484$ ) (Table 1). The ability of the Langmuir and the Elovich kinetic equations for describing PR dissolution in acid soils was also found in our previous study with a different BP (He et al., 1996a). Addition of BP, N fertilizers, and zeolite to the PR-amended soil did not affect the kinetic characteristics of PR dissolution.

Increasing BP amounts significantly decreased the initial ( $A$ ) and average dissolution rate ( $b$ ) and potential maximum dissolution of PR (PMDPR) during the the incubation period of 132 days as calculated from the Elovich and Langmuir kinetic models (Table 2). In general, AN and AS increased the initial rate, but had

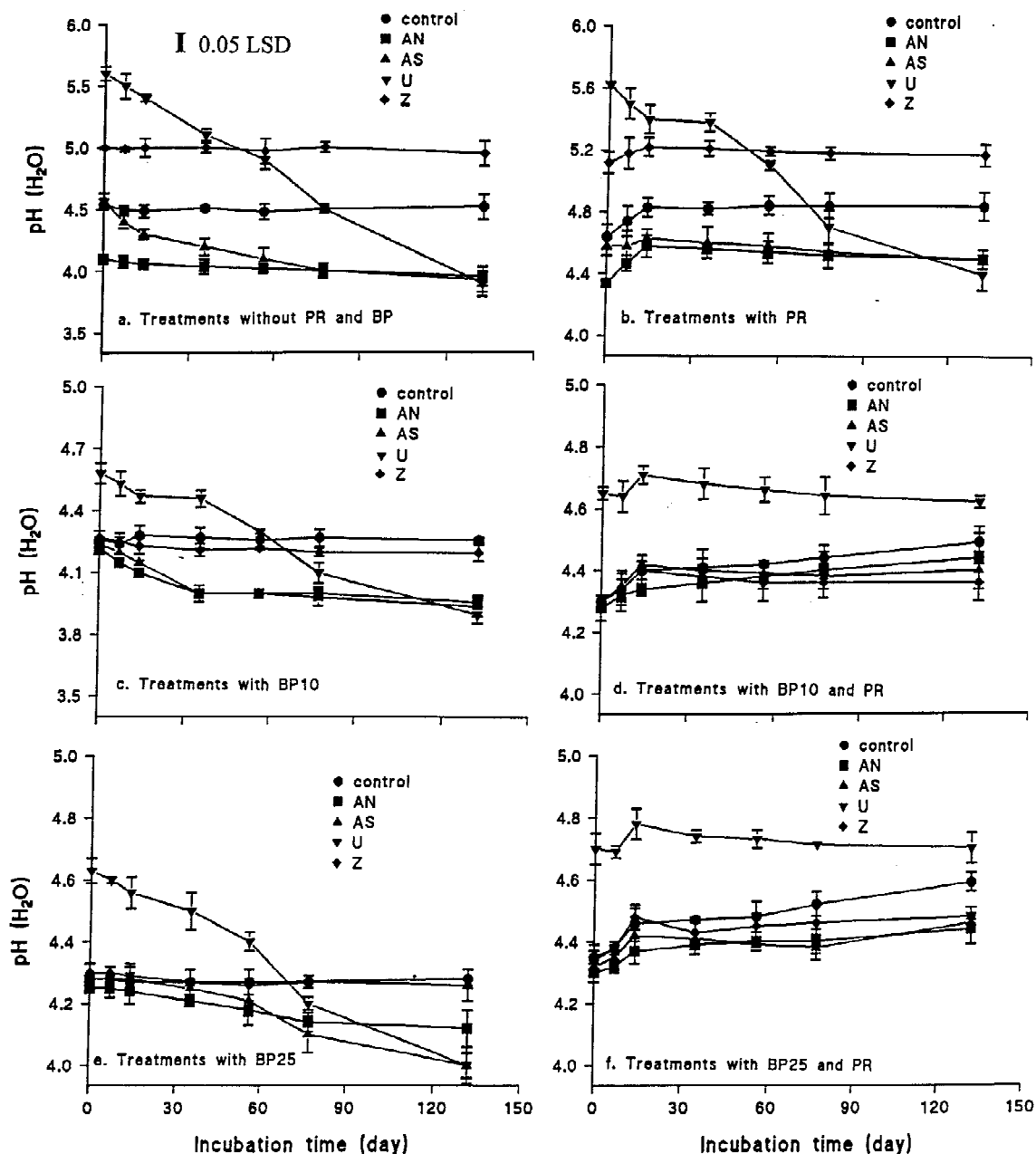


Figure 2. Effect of ammonium nitrate (AN), ammonium sulfate (AS), urea (U), and zeolite (Z) on soil pH: (a) Without BP or PR, (b) PR at 392mg P kg<sup>-1</sup> (c) BP10 at 10g kg<sup>-1</sup>, (d) BP10 and PR, (e) BP25 at 25 g kg<sup>-1</sup>, and (f) amended with BP25 and PR.

little effect (for AN) on the average PR dissolution rate (*b* value) due to a rapid but short-term acidifying effect. The AS treatment decreased *b* value compared to the control, likely due to competitive sorption between sulfate and phosphate, which might increase P concentration in soil solution and thus slowed PR dissolution over a relatively long time. On the other hand, urea

and zeolite decreased the initial rate of PR dissolution due to higher pH (Fig. 2) and increased the average PR dissolution rate because of longer and persistent acidification by urea and slow but continued removal of Ca by zeolite (Table 2). The effect of N fertilizers and zeolite on the potential maximum dissolution of PR was related to BP amounts. The PMDPR was in-

creased by the addition of AN, urea, and zeolite but was hardly affected by AS for soils without BP. Both the AN and AS increased the PMDPR, but there was no significant difference between the urea or zeolite treatment and the control for soil having received 10 g kg<sup>-1</sup> BP. However, at a higher BP amount (25 g kg<sup>-1</sup>), the PMDPR was slightly increased by the addition of urea or zeolite and less affected by the addition of AN or AS (Table 2).

#### Ratio of Olsen-P to PR-released P

After dissolution, most of the P released from PR is adsorbed by variable-charge minerals like oxides and kaolinite, resulting in a decrease of its bioavailability, with a small part of the released P remaining as available P to plants (Baligar et al., 1997). The relative proportion of the PR-P which is available to plants is related to properties of the soils. In this study, the amount of P released from PR was measured by the difference in 0.5 M NaOH-extractable P in soils with and without PR, and the increase in available P due to PR dissolution was obtained by the difference in 0.5 M NaHCO<sub>3</sub> extractable P (Olsen-P) in soils with and without PR. The PR released P increased with increasing incubation time, as did the Olsen-P (Fig. 3). Compared to the control, addition of AN and AS increased PR dissolution but decreased NaHCO<sub>3</sub> extractable P, whereas urea increased both (Fig. 3a), probably due to pH effect (Fig. 2). Similar effect of AN and urea on water extractable P in PR-amended acid soils was observed by Chien (1979), and the positive effect of urea was attributed to Ca-chelation by some products from urea hydrolysis (Chien, 1979). Addition of BP decreased the amount of Olsen-P (Fig. 3b, c) because of decreased PR dissolution (Fig. 1b, c). AN, AS, and urea increased and zeolite decreased Olsen-P for treatments receiving 10 g kg<sup>-1</sup> BP, whereas AN, urea, and zeolite increased and AS decreased Olsen-P for treatments with 25 g kg<sup>-1</sup> BP (Fig. 3b). The increase in Olsen-P for treatments receiving nitrogen fertilizers or zeolite compared to the control in the BP-amended soil was likely related to an increase in Ca associated P which is extractable to the 0.5 M NaHCO<sub>3</sub> (Smillie et al., 1987). However, the reason for the differential effect of different amounts of BP on Olsen-P for treatments receiving AS or zeolite is unknown.

Very strong relationships between Olsen-P and PR-P were observed, with determination coefficients ( $r^2$ ) ranging from 0.889 to 0.988 (data not shown). Addition of BP, N fertilizers, and zeolite did not affect the

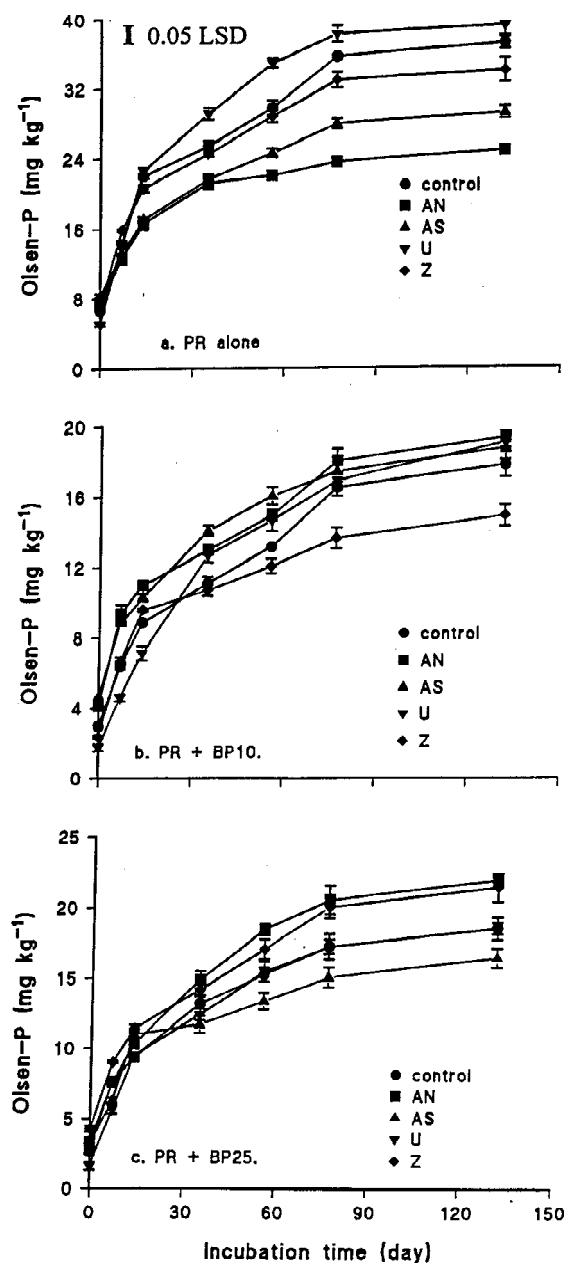


Figure 3. Effect of ammonium nitrate (AN), ammonium sulfate (AS), urea (U), and zeolite (Z) on Olsen-P in an acidic soil amended with: (a) PR at 392mg P kg<sup>-1</sup>, (b) PR + BP10 (10 g kg<sup>-1</sup>), and (c) PR + BP25 at 25 g kg<sup>-1</sup>.

fitness of the relationship between Olsen-P and PR-P to linear regression model. The ratio of the increased Olsen-P divided by total P from PR dissolution (PR-P) as determined by the 0.5 M NaOH extraction (i.e., the slope of single regression curve) varied among the

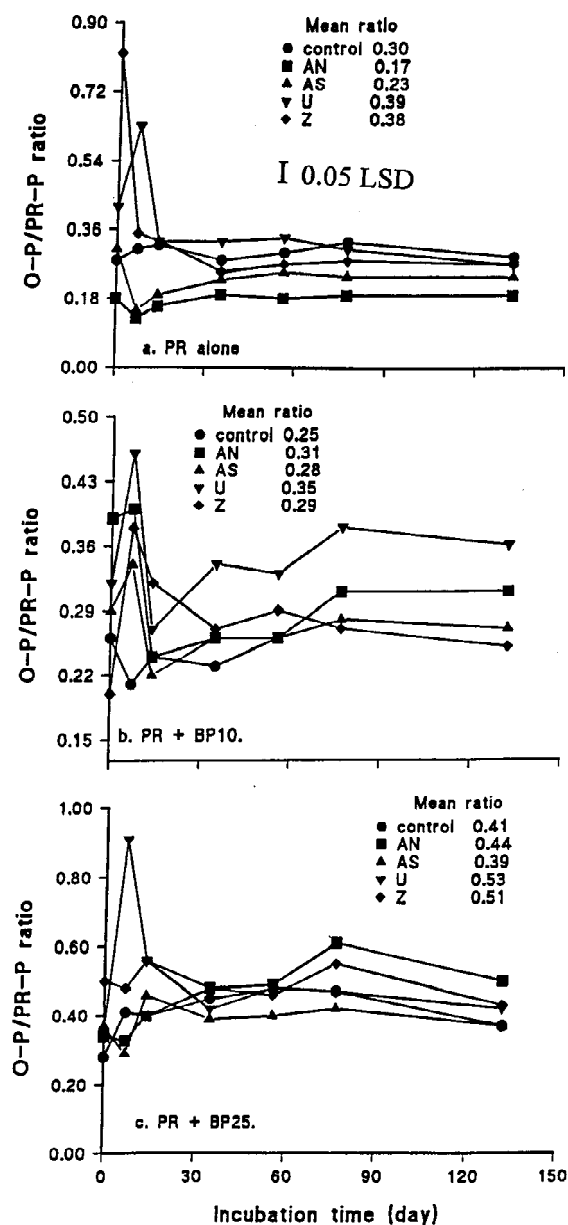


Figure 4. Effect of ammonium nitrate (AN), ammonium sulfate (AS), urea (U), and zeolite (Z) on Olsen-P/PR-P ratio in an acidic soil amended with: (a) PR at  $392\text{ mg P kg}^{-1}$ , (b) PR + BP10 (at  $10\text{ g kg}^{-1}$ ), and (c) PR + BP25 at  $25\text{ g kg}^{-1}$ .

different treatments (Fig. 4). The mean ratio of increased Olsen-P to PR-P over the whole incubation period slightly decreased by BP at  $10\text{ g kg}^{-1}$ , probably due to the decreased soil pH (Fig. 2), but increased at  $25\text{ g kg}^{-1}$ , likely because of increased Ca-P association. Compared to the control, the addition of urea

and zeolite increased the ratio of increased Olsen-P to PR-P for all of treatments with and without BP, whereas the addition of AN and AS decreased the increased Olsen-P/PR-P ratio for treatments without BP, increased it for treatments with BP at  $10\text{ g kg}^{-1}$ , and had little effect on it for soils with BP at  $25\text{ g kg}^{-1}$  (Fig. 4a-c). The increase in the ratio of increased Olsen-P to PR-P at higher amounts of BP was likely due to the association of PR-released P with Ca, which is more readily extractable to the  $\text{NaHCO}_3$ . The increase in the ratio of increased Olsen-P to PR-P by urea and zeolite was likely due to the higher pH (Fig. 2), which decreased phosphate adsorption by variable-charge minerals in soil. Similarly, the decreased Olsen-P/PR-P ratio by the addition of AN and AS likely resulted from the lower pH or more positively charged adsorption surfaces, but this negative effect was counteracted by BP additions, as Ca released from BP competed with the adsorbing surfaces for phosphate. These results indicate that amendment of BP, zeolite, and urea tended to increase the availability of the PR-released P, as shown by the ratio of increased Olsen-P to PR-P.

## Conclusions

The dissolution of PR in an acid soil consisted of an initial rapid dissolution and a slow and steady dissolution stage, which were described by both Langmuir and an Elovich-type kinetic equations. The addition of BP at  $10\text{ g kg}^{-1}$  decreased PR dissolution by approximately one-half, and at  $25\text{ g kg}^{-1}$  by two-thirds, as estimated by the PMDPR values from the Langmuir equation. The addition of AN or AS increased mainly the initial dissolution rate of PR but affected little (AN) or decreased (AS) the average dissolution rate as shown by *A* and *b* values from the Elovich equation. Overall, the addition of BP, urea, and zeolite increased the ratio of Olsen-P/PR-P, whereas the addition of AN and AS decreased the ratio in the soil without BP, but increased it in the BP-amended soil. These effects reflect complicated interactions among H, Ca,  $\text{SO}_4$ , and other soil components related to phosphorus chemistry in the amended acid soil and merit attention in the management of acid soils.

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## References

- Allen E R, Hossner L R, Ming D W and Henninger D L 1993 Solubility and cation exchange in phosphate rock and saturated clinoptilolite mixtures. *Soil Sci. Soc. Am. J.* 57, 1368–1374.
- Baligar V C, He Z L, Martens D C and Ritchey K D 1997 Effect of phosphate rock, lime, and cellulose on plant growth in acidic soil. *Plant Soil* 195, 129–136.
- Carpenter S R, Bolgrien D, Lathrop R C, Stow C A, Reed T and Wilson M A 1998 Ecological and economical analysis of lake eutrophication by nonpoint pollution. *Aust. J. Ecol.* 23, 68–79.
- Chien S H 1979 Dissolution of phosphate rock in acid soils as influenced by nitrogen and potassium fertilizers. *Soil Sci.* 127, 371–376.
- Chien S H, Clayton W R and McClellan G H 1980 Kinetics of dissolution of phosphate rocks in soils. *Soil Sci. Soc. Am. J.* 44, 260–264.
- Clark R B, Zeto S K, Ritchey K D, Wendell R R and Baligar V C 1994 Coal combustion by-product use on acid soil: effects on maize growth and soil pH and electrical conductivity. *In Waste as Resources*. Eds. D L Karlan et al. ASA and SSSA, Madison, WI.
- He Z L, Baligar V C, Martens D C, Ritchey K D 1996a Kinetics of phosphate rock dissolution in an acid soil amended with liming materials and cellulose. *Soil Sci. Soc. Am. J.* 60, 1589–1595.
- He Z L, Baligar V C, Martens D C, Ritchey K D and Kemper W D 1996b Factors affecting phosphate rock dissolution in an acid soil amended with liming materials and cellulose. *Soil Sci. Soc. Am. J.* 60, 1596–1601.
- He L M, Zelazny L W, Baligar V C, Ritchey K D and Martens D C 1997a Ionic strength effects on sulfate and phosphate adsorption on gamma-alumina and kaolinite: triple-layer model. *Soil Sci. Soc. Am. J.* 61, 784–793.
- He Z L, Baligar V C, Martens D C, Ritchey K D and Elrashidi A M 1997b Relationship of ryegrass growth to labile P in acid soil amended with phosphate rock, liming materials, and cellulose. *Agronomy Abstracts*: 233, 1997 Annual Meetings, Anaheim CA.
- Jones U S 1948 Availability of phosphorus in rock phosphate as influenced by potassium and nitrogen salts, lime, and organic matter. *J. Am. Soc. Agron.* 40, 765–770.
- Mackay A D, Syers J K, Tillman R W and Clegg P E H 1986 A simple model to describe the dissolution of phosphate rock in soils. *Soil Sci. Soc. Am. J.* 50, 291–296.
- Olsen S R, and Sommers L E (1982) Phosphorus. p.403–430. *In Methods of Soil Analysis*. Part 2, 2nd ed. Eds. A. L. Page et al. Agron. Monogr. 9. ASA and SSSA, Madison, WI.
- SAS Institute Inc. 1996 The SAS System-Release 6.12. Cary, NC, USA.
- Sikora F J and Giordano P M 1995 Future direction for agricultural phosphorus research. *Fertil. Res.* 41, 167–178.
- Smillie W G, Curtin D and Syers J K 1987 Influence of exchangeable calcium on phosphate retention by weakly acid soils. *Soil Sci. Soc. Am. J.* 51, 1169–1172.
- Thomas G W 1982 Exchangeable cations. pp 159–164. *In Methods of Soil Analysis*. Part 2, 2nd ed. Eds. A.L. Page et al. Agron. Monogr. 9, ASA and SSSA, Madison, WI.
- Tisdale S L and Nelson W L 1975 *Soil Fertility and Fertilizers*. Macmillan, New York.
- Wright R J, Baligar V C, Belesky D P and Snuffer J D 1991 The effect of phosphate rock dissolution on soil chemical properties and wheat seedling root elongation. *Plant Soil* 21, 21–30.
- Wright R J, Baligar V C and Belesky D P 1992 Dissolution of North Carolina phosphate rock in soils of the Appalachian region. *Soil Sci.* 153, 25–36.

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