



Dissolution characteristics of central Florida phosphate rock in an acidic sandy soil

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Abstract

Florida has more than 14 million ha of acidic soils and most of these acidic soils are very sandy. Transport of phosphorus from these soils to surface water is a great concern in Florida. One of the promising approaches is to develop slow release P fertilizers to replace the regular water soluble fertilizers. Dolomite phosphate rock (DPR) is an ideal material for making this type of fertilizer for acidic sandy soils, which are wide-spread in Florida. The effects of soil moisture, particle size, and source of DPR on the extent and rate of DPR dissolution in a representative acidic sandy soil were examined in an incubation study. DPR dissolution estimated by the NaOH extraction method was strongly dependent on the mineralogy and chemistry of the DPR source materials. Decreasing particle size increased the percentage dissolution of the DPR in soil. Soil moisture affected the initial dissolution rate of the DPR and the time to reach equilibrium. Soil extractable P (Olsen-P) generally increased with DPR dissolution, but the ratios of Δ Olsen-P to dissolved DPR-P (Δ NaOH-P) were significantly different between the two DPR sources. Dissolution of DPR in the acidic sandy soil was well described by the Langmuir and Elovich kinetic equations, with the Langmuir equation being better. Constant A derived from the Elovich equation and potential maximum dissolution (PMDPR) from the Langmuir equation were closely correlated with the increases in pH and exchange (Ca + Mg) after DPR application. The two parameters appeared useful in evaluating DPR dissolution and timing of DPR application in acidic sandy soils.

Introduction

Phosphorus deficiency is a major constraint to crop production in tropical and subtropical acid soils and P fertilizers are required to sustain optimum plant growth (Zapata and Zaharah, 2002). Phosphate rock (PR) has been directly applied to these soils because it is nearly as effective as water soluble superphosphate, but it is more

cost-effective for correcting P deficiencies (Rajan et al., 1991; Wright et al., 1991). In Florida, 37% of the soils are acidic with pH below 6.0 and 47% are identified as medium to low in P content (PPI-PPIC, 1998). On the other hand, large amounts of dolomite phosphate rock (DPR) materials are produced as a byproduct during processing of PR to phosphoric acid in Central Florida. These industrial byproducts contain abundant Ca, Mg, and P and can be good fertilizers for acidic sandy soils, which are deficient in

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these nutrients (Olson and Simone, 2004; Tucker et al., 1995). Otherwise, disposal of these materials could be costly to the phosphate industry.

The agronomic effectiveness of PR primarily depends on its dissolution in soils (Baligar et al., 1997). A number of kinetic equations, notably the first-order equation and Elovich equation (Sanyal and Datta, 1991), have been suggested to study kinetics of PR dissolution. Some parameters obtained from these equations are useful for adjusting the time and rate of PR application so that P released from PR dissolution could meet the demand of plant growth. PR dissolution in soils often has an initial rapid stage followed by a slower but steady stage (Syers and Mackay, 1986; Wright et al., 1992), and therefore, the Langmuir equation has been proposed for describing PR dissolution in soils (He et al., 1996a).

In addition to chemical composition and particle size, the dissolution rate of PR in soil is mainly affected by soil pH, moisture content, P and Ca concentrations in soil solution (Babare et al., 1997; Chien and Menon, 1995; Chien et al., 1980b; Kanabo and Gilkes, 1988; Smyth and Sanchez, 1982). Several studies have been conducted to evaluate the relationships between PR dissolution and soil properties that are known to influence the dissolution process (Dodor et al., 1999; He et al., 1996b). Such information can enhance the selection procedure for the most appropriate PR for a particular soil and be used to develop models for assessing PR dissolution (Hughes and Gilkes, 1986b).

Most of the agricultural land in Florida is on extremely coarse-textured sand, with sand content often in excess of 90% (Hoogeweg and Hornsby, 1997). Studies on the solubility and agricultural effectiveness of PR have become important for developing slow release PR fertilizers due to low P retention capacity and high P leaching potential of the coarse-textured soils (He et al., 1999). Unfortunately, minimal information is available on PR dissolution in the acidic sandy soils in Florida. This study was carried out to investigate the effects of source, particle size, and soil moisture content on the dissolution rate of Central Florida DPR in an acidic sandy soil. The relationships between quantitative kinetic parameters of DPR dissolution and changes of major

soil properties were evaluated. The objective was to understand the reactions of DPR in acidic sandy soils and to generate information needed for developing DPR-based slow release P fertilizer.

Materials and methods

Soil and dolomite phosphate rock (DPR) materials

A typical acidic sandy soil (Wabasso: sand 96.1%, silt 2.3%, and clay 1.6%) classified as hyperthermic alfic haplaquods, was collected from the 0–40 cm layer in Fort Pierce, Florida. Wabasso sand is a representative soil used for commercial citrus and vegetable production in the area. The collected soil was air-dried and passed through a 2.0 mm sieve. Selected properties of the soil were 5.0 g kg⁻¹ organic C, 0.23 g kg⁻¹ total N, 4.1 pH (1:1 H₂O), 3.2 pH (1:1 KCl), 5.1 mg NaOH extractable P kg⁻¹ soil, 0.6 mg Olsen-P kg⁻¹ soil, 30 µg g⁻¹ microbial biomass C, and 0.38 cmol kg⁻¹ 1.0 M NH₄OAc exchangeable(Ca + Mg).

Samples of two dolomite phosphate rock (DPR) sources, i.e., IDPR and CDPR, were obtained from two different operating phosphate mines in Central Florida. The DPR is a by-product from phosphate industry, which contains too high dolomite to be used for processing phosphoric acid. The DPR may also contain small amount of phosphatic clay, depending upon the location. The samples were ground to <0.149 mm for chemical analysis and following studies. The relevant mineralogical and chemical properties of the DPR samples are presented in Table 1. Total concentrations of P, Ca, Mg, Fe, K, and Al in the DPR samples were determined by digesting the sample with HCl–HNO₃ and analyzing the digester for elemental concentrations using inductively coupled plasma atomic emission spectrometry (ICP-AES, Ultima, JY Horiba Inc. Edison, NJ). pH and electrical conductivity (EC) were measured in water at a soil:solution ratio of 1:1 using a pH/Ion/EC meter (Accumet model 50, Fisher Scientific, Atlanta, GA). NaOH extractable P was determined by extracting the DPR sample with 0.5 M NaOH at a 1:50 soil:solution ratio for

Table 1. Chemical composition, CaCO₃ equivalent, and other relevant properties of the two DPR sources from Central Florida

Characteristics	IDPR	CDPR
pH (H ₂ O)	7.2 ± 0.0	7.7 ± 0.0
EC (μs cm ⁻¹)	472 ± 33	578 ± 53
Total P (g kg ⁻¹)	96 ± 1	103 ± 2
NaOH extractable P (g kg ⁻¹)	7.15 ± 0.5	0.006 ± 0
NaHCO ₃ extractable P (mg kg ⁻¹)	173 ± 11	109 ± 14
Neutral ammonium citrate extractable P (g kg ⁻¹)	1st extraction: 6.9 ± 0.4 2nd extraction: 5.4 ± 0.5	1st extraction: 0.011 ± 0 2nd extraction: 0.04 ± 0
2% citric acid extractable P (g kg ⁻¹)	1st extraction: 35.6 ± 1.1 2nd extraction: 16.2 ± 0.1	1st extraction: 2.49 ± 0 2nd extraction: 2.27 ± 0.03
Total Ca (g kg ⁻¹)	248 ± 4	308 ± 1
Total Mg (g kg ⁻¹)	8.0 ± 0.8	14.5 ± 1.2
Total K (g kg ⁻¹)	0.84 ± 0.0	0.62 ± 0.1
CaCO ₃ Equivalent (%)	62 ± 1	77 ± 0
Total Fe (g kg ⁻¹)	8.4 ± 0.5	7.0 ± 0.6
Total Al (g kg ⁻¹)	5.2 ± 0.2	4.2 ± 0.1
Mineral composition	Francolite, quartz, phosphatic clay, calcite, dolomite	Francolite, quartz, calcite, dolomite

16 h and P concentration in the extract determined by the ascorbic acid reduction-molybdenum blue method (He et al., 1996a/b). The neutral ammonium citrate (NAC) or 2% citric acid (AC) extractable P was measured by successively extracting the DPR sample with NAC or CA twice and P concentrations in the extracts were measured using a modified ascorbic acid reduction-molybdenum blue method (He et al., 1998). The calcium carbonate equivalent of the DPR samples was determined by the AOAC method (Kane, 1995). Subsamples were further ground to <0.106 or <0.053 mm for particle size evaluation prior to the incubation experiment.

Incubation experiment

The treatments of this study consisted of three particle sizes (<0.149, <0.106, and <0.053 mm), two DPR sources (IDPR, CDPR), and three levels of soil moisture content (30, 70, and 100% water-holding capacity). Portions of soil were weighed and thoroughly mixed with DPR at 400 mg P kg⁻¹ soil. Controls (without amendments) were prepared for each level of soil moisture content. The total weight of each soil-amendment mixture was 0.35 kg (oven-dry basis). The mixture was

placed in 1 L plastic containers and incubated in a temperature-controlled chamber at 25 °C. There were three replicates for each treatment and all the containers were randomly arranged with a split factorial design. The moisture content of the mixture was weighed every other day and water was added to compensate any evaporation loss. At the intervals of 1 d (sampled on the same day as being prepared), 7 d, 20 d, 40 d, 60 d, 80 d of incubation, subsamples in three replicates were taken for measurements of DPR dissolution. Soil pH and exchangeable cations were determined at the end of incubation.

DPR dissolution was measured by a modified 0.5 NaOH extraction method (Alloush, 2003; He et al., 1996a). In this procedure, P released from PR dissolution is assumed to be mostly adsorbed by sesquioxides, oxides, or precipitated as Fe and Al phosphates in the acidic soil, where both the adsorbed P and newly formed Fe and Al phosphates can be extracted into the 0.5 M NaOH solution through desorption or solubilization. Consequently, the differences in the P levels (ΔP) between DPR treated soil and the control samples were used as an estimate of DPR dissolution after accounting for the NaOH extractable P in the original DPR samples. Soil Olsen-P

(0.5 M NaHCO₃ extraction method), as an important index of plant available P, was also determined during incubation. Phosphorus in both NaOH and Olsen-P extracts was determined colorimetrically by an ascorbic-molybdate method (Olsen and Sommers, 1982). The Olsen-P in the original DPR samples was <1% of the total extractable P from the DPR amended soil and was therefore negligible.

Soil pH was measured in water and 1 M KCl solution at a soil:solution ratio of 1:1 using the pH/Ion/EC meter. Exchangeable Ca and Mg were extracted with 1.0 M NH₄OAc and determined using the ICP-AES.

Kinetic description

Three kinetic equations, i.e., the first-order, Elovich, and Langmuir equations, were used to quantify the treatment effect on DPR dissolution in soil.

The first-order reaction is expressed as follows:

$$\ln C_t = \ln C_0 - kt,$$

where C_0 is the initial amount of DPR added, C_t is the amount of residual DPR (as a fraction of DPR added) at time t (d). When $C_t = 1/2C_0$, $t_{1/2}$ (half-life) = $0.693/K$.

Derivation of the Elovich equation results in a simplified form of the equation:

$$\Delta P = C_0 - C_t = (1/\beta)\ln(\alpha\beta) + (1/\beta)\ln(t)$$

The above equation can be further simplified by assigning $a = C_0 - (1/\beta)\ln(\alpha\beta)$ and $b = 1/\beta$, i.e., $C_t = a - b \ln(t)$

Since constant a is the amount of residual DPR (as a fraction of the added DPR), the quantity $(1 - a)$, which can be designated as A , can be defined as the initial dissolution rate of DPR. Constant b (the slope) is related to the average rate of DPR dissolution from 1 d to the end of incubation.

The linear form of the Langmuir kinetic equation is:

$$t/q = a + bt,$$

where q is the amount of P (g kg^{-1} mg) released from DPR at time t (d), a and b are constants with $b = 1/q_m$, where q_m is defined as the potential maximum dissolution of DPR (PMDPR).

Results

The IDPR or CDPR material is composed predominantly of francolite (carbonate-fluorapatite), and variable amounts of quartz, phosphatic clay and free dolomite and calcite. The CDPR contained more free dolomite and calcite as indicated by its higher calcium carbonate equivalence than the IDPR (Table 1). Since these samples contained <1% of total Fe or total Al (Table 1), the amounts of Fe and Al phosphates in the samples if present were minimal. The CDPR only contained 0.006 g kg^{-1} 0.5 M NaOH extractable P. However, the IDPR sample appeared to have a considerable amount of phosphatic clay. The major component of the phosphatic clay is small particle size francolite, but there were also small amounts of silicate minerals such as kaolinite, quartz, and smectite and small amounts of Fe and Al oxides. Therefore, the IDPR contained more NaOH extractable P (7.15 g kg^{-1}) than the CDPR, because some P released during PR processing may be retained by the kaolinite or oxides in the phosphatic clay and desorbed during the NaOH extraction.

The IDPR and CDPR contained similar amount of total P (96 and 103 g kg^{-1} , respectively), but the IDPR had more extractable P as determined by the neutral ammonium citrate (NAC) or the 2% citric acid (CA) method (Table 1). The low solubility of CDPR-P in either NAC or Ac was likely due to some free calcite and dolomite contained in the CDPR sample, as indicated by its high CCE, which is about 17% higher than the theoretical value (61% for francolite from Central Florida) (Sikora, 2002). The IDPR had a CCE% of 62, which is close to its theoretical value (61%). However, recent study by Sikora (2002) revealed that the AOAC method underestimated CCE% of phosphate rock due to possible formation of CaHPO₄. He also pointed out that the AOAC method may not be suitable for determining %CCE for PR because it did not accurately represent the reactions and reaction products that would occur upon dissolution in soil and it would not represent actual conditions whereby PR dissolution is incomplete. Therefore, the IDPR sample might also contain a small amount of free dolomite and calcite, which is expected, because these DPR materials were considered to

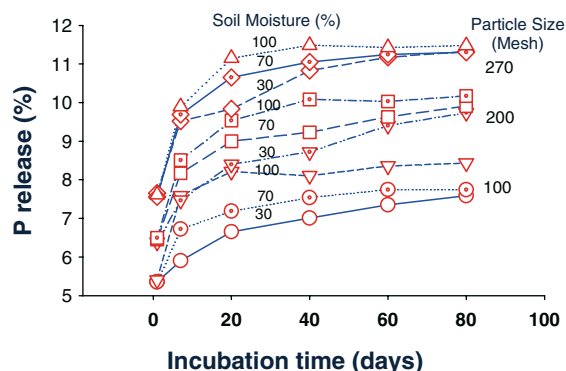


Figure 1. Percentage dissolution of IDPR in laboratory incubated soil as affected by particle size and soil moisture condition.

be not suitable for manufacturing phosphoric acid because of their relatively high dolomite contents. The total NAC extractable P accounted for 12.8% of the total P in the IDPR, but only 0.01% in the CDPR. The low solubility of P in the CDPR is likely related to its high calcite or dolomite. In addition, the NAC extraction has been observed to be relatively inefficient in dissolving basic Ca phosphates such as francolite (Lehr, 1980). More P was extracted into the CA reagent due to its acidity and up to 50% of the total P in the IDPR was dissolved in the CA, but the corresponding value was <5% for the CDPR (Table 1). Therefore, IDPR seems superior to the CDPR in providing available P.

The percentages of DPR dissolution estimated by the 0.5 M NaOH extraction method (ΔP , increase in extractable P), averaged for triplicate soil samples, are presented in Figures 1 and 2. The dissolution of the IDPR or CDPR was rapid, and from 5 to 8% of the total P was released from the IDPR in the first day of the incubation after accounted for the 7.4% NaOH extractable P and the corresponding value was 5–6% for the CDPR. This was expected because the predominant phosphates in the PR were carbonate-fluorapatites and the sandy soil contained mainly active acidity. The slightly higher percentages of P release from the IDPR than the CDPR mainly resulted from greater amounts of free dolomite and calcite in the CDPR that consumed a portion of the soil acidity. The small amount of phosphatic clay (approximately 5%) in the IDPR may also contribute to the enhanced P release because of quick dissolution of small par-

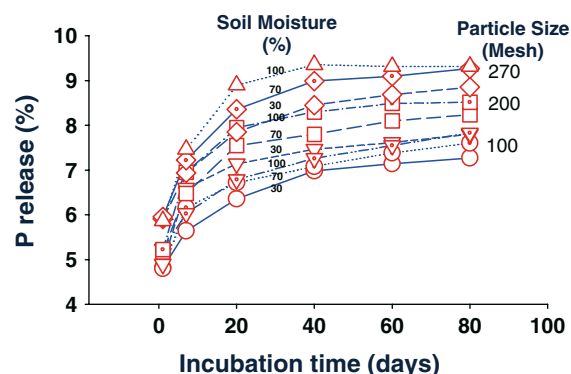


Figure 2. Percentage dissolution of CDPR in laboratory incubated soil as affected by particle size and soil moisture condition.

ticle size francolite in the clay fraction and P desorption from the clay surface.

In general, the DPR dissolution increased with incubation time in the first 20 d, and then the dissolution rate leveled off.

There were differences in the extent of DPR dissolution between the two sources. Approximately 12% of the added IDPR was dissolved in the finest (<0.053 mm) phosphate rock treatment at 80 d, and 9% of the added CDPR was dissolved during the period. These differences agree with their P solubility characteristics measured by the NAC or CA method.

The effect of particle size or fine grinding on DPR dissolution was evident (Figures 1 and 2). For the soil treated with the finest IDPR (<0.053 mm), percentage dissolution increased by 3–4%, as compared with that of the <0.149 mm particle size. Since only a small amount of CDPR was dissolved for each treatment, decreasing particle size had only minimal effects on the percentage dissolution of CDPR in the soil.

Soil moisture content had significant effects on DPR dissolution (Figures 1 and 2). Throughout the entire incubation period, the extent of DPR dissolution followed the order: 100% water-holding capacity (WHC) > 70% WHC > 30% WHC, although the discrimination in DPR dissolution among the treatments was not consistent. DPR dissolution from 20 d to the end of incubation appeared to decrease steadily because most of readily dissolved DPR was depleted in the first 20 d after incubation in the soil with higher moisture content. These results

Table 2. Fitness of various kinetic models for describing DPR dissolution in an acidic sandy soil

Treatment	First-order reaction $\ln C_t = \ln C_0 - kt$		Elovich equation $C_t = a - b \ln t$		Langmuir equation $t/q = a + bt$	
	r^2	SD	r^2	SD	r^2	SD
IDPR						
<0.149 mm 30%WHC	0.894**	0.002	0.839*	0.002	0.999***	0.007
<0.149 mm 70%WHC	0.650	0.004	0.985***	0.000	0.999***	0.004
<0.149 mm 100%WHC	0.485	0.005	0.981***	0.001	0.999***	0.003
<0.106 mm 30%WHC	0.885**	0.003	0.882**	0.002	0.998***	0.009
<0.106 mm 70%WHC	0.732*	0.004	0.980***	0.001	0.999***	0.006
<0.106 mm 100%WHC	0.634	0.006	0.980***	0.001	0.999***	0.003
<0.053 mm 30%WHC	0.784*	0.004	0.948***	0.002	0.999***	0.006
<0.053 mm 70%WHC	0.643	0.007	0.988***	0.001	0.999***	0.044
<0.053 mm 100%WHC	0.556	0.006	0.975***	0.001	0.999***	0.002
CDPR						
<0.149 mm 30%WHC	0.822*	0.002	0.899**	0.002	0.998***	0.031
<0.149 mm 70%WHC	0.758*	0.003	0.980***	0.001	0.998***	0.033
<0.149 mm 100%WHC	0.656	0.004	0.997***	0.000	0.999***	0.021
<0.106 mm 30%WHC	0.856**	0.002	0.885**	0.002	0.997***	0.036
<0.106 mm 70%WHC	0.728*	0.004	0.953***	0.001	0.999***	0.023
<0.106 mm 100%WHC	0.642	0.004	0.980***	0.001	0.999***	0.014
<0.053 mm 30%WHC	0.816*	0.003	0.925**	0.002	0.999***	0.022
<0.053 mm 70%WHC	0.748*	0.004	0.939**	0.002	0.999***	0.018
<0.053 mm 100%WHC	0.636	0.005	0.943**	0.002	0.999***	0.013

*, **, *** Significant at 0.05, 0.01, and 0.001 levels of confidence, respectively ($n = 6$).

SD: Standard Deviation.

indicate that DPR dissolution requires a much longer time to reach relative equilibrium in a soil with lower moisture content, as compared with higher moisture content.

The Langmuir and Elovich kinetic equations fit well the dissolution of DPR (Table 2), especially the Langmuir equation. The first-order kinetic reaction was not adequate for describing DPR dissolution in soils as evidenced by the fact that the half-life ($t_{1/2}$) of DPR calculated from the first-order equation in all the treatments were longer than 1400 d, and the differences between treatments of different moisture contents or DPR sources could not be discriminated by the $t_{1/2}$ (Table 3). Both A and b values, which were obtained from the Elovich equation, increased with increasing soil moisture or finer particle size. The value of A ranged from 0.120 to 0.151 in the IDPR treatments, and from 0.042 to 0.057 in the CDPR treatments. These results suggest that the source of DPR could considerably affect its initial dissolution. All the PMDPR values of IDPR treatments were much higher than those of CDPR treatments. These results agreed with the

observation of increased NaOH extractable P during the incubation. For example, PMDPR in the <0.106 mm IDPR treatments was 10–16% higher than that in <0.149 mm treatments. On the other hand, an increase in PMDPR accompanying an increase in soil moisture content (Table 3) indicated that soil moisture is another important factor that affects DPR dissolution.

An increased PR dissolution in soils does not guarantee an increase in the amount of plant available P (Sanyal and Datta, 1991). Soil Olsen-P was also determined due to a close relationship between the amount of Olsen-P and P taken up by plants. Olsen-P in the soils amended with DPR showed a similar trend as NaOH extractable P. The Langmuir and Elovich kinetic equations were also adequate for describing the increase in Olsen-P. The three DPR dissolution kinetic parameters, i.e., A , b and PMDPR, consistently increased with reduced particle size or increased soil moisture content (data not shown).

The availability index of DPR dissolution, as estimated by the ratio of Δ Olsen-P (Olsen-P in the DPR amended soil minus Olsen-P in the

Table 3. Kinetic parameters ($t_{1/2}$, A , b and PMDPR from kinetic models) of DPR dissolution in an acidic sandy soil estimated by NaOH extraction

Treatment	$t_{1/2}$ d	A fraction of DPR d^{-1}	b fraction of PR $(\ln d)^{-1}$	PMDPR mg P kg^{-1}
IDPR				
<0.149 mm 30%WHC	2326	0.1198	0.0032	54.9
<0.149 mm 70%WHC	2520	0.1227	0.0037	55.9
<0.149 mm 100%WHC	2318	0.1268	0.0046	58.1
<0.106 mm 30%WHC	1586	0.1331	0.0047	63.7
<0.106 mm 70%WHC	1715	0.1362	0.0050	64.1
<0.106 mm 100%WHC	1631	0.1386	0.0057	65.4
<0.053 mm 30%WHC	1494	0.1485	0.0054	70.4
<0.053 mm 70%WHC	1586	0.1495	0.0058	69.9
<0.053 mm 100%WHC	1585	0.1513	0.0061	70.9
CDPR				
<0.149 mm 30%WHC	2341	0.0419	0.0037	24.4
<0.149 mm 70%WHC	2295	0.0435	0.0041	25.5
<0.149 mm 100%WHC	2365	0.0459	0.0043	26.2
<0.106 mm 30%WHC	2235	0.0459	0.0037	26.5
<0.106 mm 70%WHC	2026	0.0481	0.0046	28.2
<0.106 mm 100%WHC	1965	0.0510	0.0051	29.4
<0.053 mm 30%WHC	1963	0.0542	0.0044	30.7
<0.053 mm 70%WHC	1786	0.0563	0.0051	32.5
<0.053 mm 100%WHC	1805	0.0574	0.0055	32.7

$t_{1/2}$ = the half-life of DPR in first-order rate equation ; A = the initial dissolution rate of DPR in Elovich equation; b = the average dissolution rate of DPR from 1 to 80 d in Elovich equation and PMDPR = potential maximum dissolution of DPR in Langmuir equation.

control) to Δ NaOH-P, showed significant discrimination between the two sources of DPR for all treatments. The availability index in the IDPR-amended soil was 24.8% based on the regression equation, whereas that in the CDPR-amended soil was 48.6%. This difference is likely associated with the nature and composition of the two DPR sources.

Soil properties such as pH, exchange Ca and Mg, are key factors related to PR dissolution in soil (He et al., 1996b). The application of DPR materials raised soil pH (water or KCl) and increased exchangeable (Ca + Mg). The liming effect of CDPR is much greater than that of IDPR. Soil pH (water) ranged from 4.9 to 5.3 in the IDPR treatments, and from 5.4 to 6.3 in the CDPR treatments. The influence of DPR dissolution on these soil properties was also indicated by a linear regression analysis (Table 4). The results showed that changes of these soil properties were highly correlated with the DPR dissolution kinetic parameters ($t_{1/2}$, A , b and PMDPR). In comparison, changes of soil pH (water or KCl)

and exchangeable (Ca + Mg) were more closely related with A and PMDPR than with b and $t_{1/2}$.

Discussion

The dissolution of PR is strongly dependent on the mineralogy and chemistry of the DPR source materials (Hammond et al., 1986; Khasawneh and Doll, 1978). It is well established that the extent of PR dissolution increases with the degree of carbonate substitution and Ca:P ratio of apatite in the PR (Bolland et al., 1997; Hughs and Gilkes, 1986a). However, in the present study, the percentage dissolution for CDPR was lower than that for IDPR although CDPR had higher Ca:P ratio (Table 1). This suggests that the amounts of free calcium and magnesium carbonate contents in the two DPR sources may be different, as evidenced by the difference in soil pH changes caused by IDPR and CDPR treatments. The greater liming effect of CDPR raised soil pH more, and consequently decreased the dissolution

Table 4. Correlation coefficients (*r*) between DPR dissolution kinetic parameters and soil properties

Properties	IDPR				CDPR			
	$t_{1/2}$	<i>A</i>	<i>b</i>	PMDPR	$t_{1/2}$	<i>A</i>	<i>b</i>	PMDPR
$\Delta\text{pH}(\text{H}_2\text{O})$	-0.912***	0.958***	0.884**	0.975***	-0.896**	0.956***	0.686*	0.944***
$\Delta\text{pH}(\text{KCl})$	-0.834**	0.966***	0.954***	0.956***	-0.956***	0.984***	0.811**	0.986***
$\Delta\text{Exchangeable}(\text{Ca}^+\text{Mg})$	-0.891**	0.979***	0.960***	0.979***	-0.950***	0.950***	0.751*	0.958***

*, **, *** Significant at 0.05, 0.01, and 0.001 levels of confidence, respectively ($n = 9$).

$\Delta\text{pH} = \text{pH increase after DPR application}$; $\Delta\text{Exchangeable}(\text{Ca} + \text{Mg}) = \text{Exchangeable}(\text{Ca} + \text{Mg}) \text{ increase after DPR application}$.

extent of CDPR because a portion of soil acidity was consumed by the free carbonates.

Usually, decreasing particle size increases the rate of dissolution and agronomic effectiveness of PR (Bolland and Gilkes, 1989; Rajan et al., 1992). Finely ground PR has a large specific surface area, which provides a good contact between PR particles and soil solution, thereby enhancing the rate of chemical reaction between hydrogen ions in soil solution and PR (Bolland et al., 1997; Kanabo and Gilkes, 1987). As expected, our results showed that there was a consistent increase in percentage dissolution and in the three dissolution parameters (*A*, *b* and PMDPR) with a decrease in particle sizes.

Soil moisture content is another important factor that affects PR dissolution due to increased availability of water for PR dissolution and a decrease in concentration of Ca^{2+} and H_2PO_4^- ions accompanying an increase in soil moisture content (Debnath and Basak, 1986; Mackay et al., 1986). In this respect the three parameters (*A*, *b*, and PMDPR) demonstrate that the overall dissolution of DPR is greater in higher moisture content. However, our results did not show a consistent change in the half-time ($t_{1/2}$) of DPR. Furthermore, the increase in DPR dissolution from 20 to 80 d diminished with increasing soil moisture content. The decreased soil moisture content, though slowing DPR dissolution, prolonged the period of DPR dissolution, as compared with the higher moisture content treatments. These results imply that it is possible to adjust DPR dissolution to meet the P demand of plants in acidic sandy soils by controlling soil moisture content.

Several models have been successfully used to describe PR dissolution in soils. The first-order reaction is the simplest model, and the physical meaning of the constant ($t_{1/2}$) is well defined

(Sanyal and Datta, 1991). Chien et al. (1980a) fitted their data to some kinetic models and concluded that an Elovich equation gave the best fit. More recently, the Langmuir equation was also proposed for describing PR dissolution in soils (He et al., 1996a). The high $t_{1/2}$ values from the first-order equation suggest that DPR dissolution in the acidic sandy soil may be slow due to limited soil acidity, although the DPR dissolution was very rapid during the first day of incubation, as indicated by the high *A* values from the Elovich equation. The tested soil had high sand, low organic matter content and microbial biomass, and minimal buffering capacity. This may be the reason why the Langmuir kinetic equation appeared better than any other model for describing DPR dissolution in the acidic sandy soil. This is in good agreement with the observation made by He et al. (1996a). Another advantage of the Langmuir equation over other models is that a PMDPR can be obtained and used for comparing the potential of DPR dissolution in different soils or under different conditions. The Langmuir equation appeared to be the best model for evaluating DPR dissolution and application in acidic sandy soils.

Phosphorus released from PR dissolution can be sorbed by sesquioxides, oxides, or precipitated as Fe and Al phosphates in acid soil, whereas only a fraction of dissolved P becomes available for plant uptake. Several extractants have been used to measure increases in solution P during PR dissolution (Apthorp et al., 1987; Bolan and Hedley, 1989). Numerous studies demonstrated close relationships between Olsen-P and P uptake by plants, but NaHCO_3 extractable P often underestimates PR dissolution (Alloush, 2003). The use of 0.5 M NaOH as an extractant was found to be better than 0.5 M NaHCO_3 and 1 M NH_4OAc , particularly when soil organic P

formation is negligible (Sanyal and Datta, 1991). The sorbed P and newly formed Fe and Al phosphates can be mostly extracted into 0.5 M NaOH, but only a fraction can be extracted by the NaHCO₃. Therefore, the increase in NaOH extractable P was much higher than the increase in Olsen-P in the soils amended with DPR. Furthermore, due to difference in their chemical characteristics of the two DPR sources (e.g. the contents of Ca and Mg), the availability index (the ratio of ΔOlsen-P to ΔNaOH-P) of IDPR was much lower than that of CDPR.

The capacity of a soil to supply hydrogen ions, as estimated by soil pH and the exchangeable acidity, is the most important factor that controls PR dissolution (Bolland et al., 1997; Gilkes and Bolland, 1990). PR dissolution increases soil pH, which resulted from the consumption of protons in the reaction, e.g., $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 12\text{H}^+ \rightarrow 10\text{Ca}^{2+} + 6\text{H}_2\text{PO}_4^- + 2\text{F}^-$ (Khasawneh and Doll, 1978; Lewis et al., 1997). Dissolution of PR also releases Ca and Mg as the reaction products in proportion to the rate of P release. Consequently, changes in the pH (water or KCl) and exchangeable (Ca + Mg) can be used as indirect estimate of the extent of PR dissolution. In this respect, our result demonstrated that the correlations between the three soil properties and PMDPR or *A* were better than that between the soil properties and *b* or *t*_{1/2}, indicating that PMDPR and *A* can serve as more comprehensive indicators of the kinetics of DPR dissolution and are useful for predicting DPR dissolution and utilization in acidic sandy soils.

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References

- Alloush G A 2003 Dissolution and effectiveness of phosphate rock in acidic soil amended with cattle manure. *Plant Soil* 251, 37–46.
- Apthorp J N, Hedley M J and Tillman R W 1987 The effects of nitrogen fertilizer form on the plant availability of phosphate from soil, phosphate rock and monocalcium phosphate. *Fert. Res.* 12, 269–284.
- Babare A M, Sale P W G, Fleming N, Garden D L and Johnson D 1997 The agronomic effectiveness of reactive phosphate rock. V. The effect of particle size of a moderately reactive phosphate rock. *Aust. J. Exp. Agric.* 37, 969–984.
- Baligar V C, He Z L, Martens D C, Ritchey K D and Kemper W D 1997 Effect of phosphate rock, coal combustion byproduct, lime and cellulose on plant growth in an acidic soil. *Plant Soil* 195, 129–136.
- Bolan N S and Hedley M J 1989 Dissolution of phosphate rocks in soils. 1. Evaluation of extraction methods for the measurement of phosphate rock dissolution. *Fert. Res.* 19, 65–75.
- Bolland M D A and Gilkes R J 1989 Reactive rock phosphate fertilizers and soil testing for phosphorus: The effect of particle size on the rock phosphate. *Fert. Res.* 21, 75–93.
- Bolland M D A, Lewis D C, Gilkes R J and Hamilton L J 1997 Review of Australian phosphate rock research. *Aust. J. Exp. Agric.* 37, 845–859.
- Chien S H and Menon R G 1995 Factors affecting the agronomic effectiveness of phosphate rock for direct application. *Fert. Res.* 41, 227–234.
- Chien S H, Clayton W R and McClellan G H 1980a Kinetics of Dissolution of phosphate rocks in soils. *Soil Sci. Soc. Am. J.* 44, 260–264.
- Chien S H, Leon L A and Tejada H R 1980b Dissolution of North Carolina phosphate rock in acid Colombian soils as related soil properties. *Soil Sci. Soc. Am. J.* 44, 1267–1271.
- Debnath N C and Basak R K 1986 Effect of rock phosphate and basic slag on available phosphorus in acid soils in relation to soil characteristics, seasons, and moisture regimes. *J. Indian Soc. Soil Sci.* 34, 464–470.
- Dodor D E, Oya K, Tokashiki Y and Shimo M 1999 Dissolution of phosphate rock fertilizers in some soils of Okinawa, Japan. *Aust. J. Soil Res.* 37, 115–124.
- Gilkes R J and Bolland M D A 1990 The poor performance of rock phosphate fertilizers in Western Australia. Part 2. The soil chemical explanations. *Agr. Sci.* 3, 44–47.
- Hammond L L, Chien S H and Mokwunye A U 1986 Agronomic value of unacidulated and partially acidulated phosphate rocks indigenous to the tropics. *Adv. Agron.* 40, 89–140.
- He Z L, Alva A K, Li Y C, Calvert D V and Banks D J 1999 Sorption-desorption and solution concentration of phosphorus in a fertilized sandy soil. *J. Environ. Qual.* 28, 1804–1810.
- He Z L, Baligar V C, Martens D C, Ritchey K D and Kemper W D 1996a Kinetics of phosphate rock dissolution in an acidic 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 acid soil amended with liming materials and cellulose. *Soil Sci. Soc. Am. J.* 60, 1596–1601.
- He Z L, Baligar V C, Martens D C, and Ritchey K D 1998 Determination of soluble phosphorus in the presence of organic ligands or fluoride. *Soil Sci. Soc. Am. J.* 62, 1538–1541.

- Hoogeweg C G and Hornsby A G 1997 Simulated effects of irrigation practices on leaching of citrus herbicides in Flatwoods and Ridge-type soils. *Soil Crop Sci. Soc. Fla. Pro.* 56, 98–108.
- Hughes J C and Gilkes R J 1986a The effect of rock phosphate properties on the extent of fertilizer dissolution in soils. *Aust. J. Soil Res.* 24, 209–217.
- Hughes J C and Gilkes R J 1986b The effect of soil properties and level of fertilizer application on the dissolution of Sechura rock phosphate in some soils from Brazil, Colombia, Australia, and Nigeria. *Aust. J. Soil Res.* 24, 219–227.
- Kanabo I A K and Gilkes R J 1987 The role of soil pH in the dissolution of phosphate rock fertilizers. *Fert. Res.* 12, 165–174.
- Kanabo I A K and Gilkes R J 1988 The effects of moisture regime and incubation period on the dissolution of North Carolina phosphate rock in soil. *Aust. J. Soil Res.* 26, 153–163.
- Kane P F 1995 Agricultural liming materials. *In* Official Methods of Analysis of AOAC International. Ed. P Cunniff. AOAC International, Arlington, VA.
- Khasawneh F E and Doll E C 1978 The use of phosphate rock for direct application to soils. *Adv. Agron.* 30, 159–206.
- Lehr J R 1980 Phosphate raw materials and fertilizers: Part I-A look ahead. *In* The Role of Phosphorus in Agriculture. Eds. F E Khasawneh, E C Sample and E J Kamparath. pp. 81–120. ASA and SSSA, Madison, WI.
- Lewis D C, Hindell R P and Hunter J 1997 Effects of phosphate rock products on soil pH. *Aust. J. Exp. Agric.* 37, 1003–1008.
- Mackay A D, Syers J K, Tillman R W and Gregg P E H 1986 A simple model to describe the dissolution of phosphate rock in soil. *Soil Sci. Soc. Am. J.* 50, 291–296.
- Olsen S R and Sommers L E 1982 Phosphorus. *In* Methods of Soil Analysis. Ed. A L Page. pp. 403–430. ASA and SSSA, Madison, WI.
- Olson S M and Simonne E (Ed) 2004 Vegetable Production Guide for Florida. University of Florida, Gainesville, FL.
- Potash and Phosphate Institute / Potash and Phosphate Institute of Canada (PPI/PPIC) 1998 Soil test phosphorus, potassium, and pH in North America. Technical Bulletin of PPI/PPIC, Saskatoon, Canada.
- Rajan S S S, Brown M W, Boyes M K and Upsdell M P 1992 Extractable phosphorus to predict agronomic effectiveness of ground and unground phosphate application. *Fert. Res.* 32, 291–302.
- Rajan S S S, Fox R L, Saunders W M H and Upsdell M 1991 Influence of pH, time, and rate of application on phosphate rock dissolution and availability of pasture. I. Agronomic benefits. *Fert. Res.* 28, 85–93.
- Sanyal S K and Datta S K D 1991 Chemistry of phosphorous transformations in soil. *Adv. Soil Sci.* 16, 1–94.
- Sikora F J 2002 Evaluating and quantifying the liming potential of phosphate rocks. *Nutri. Cycl. Agroecosys.* 63, 59–67.
- Smyth T J and Sanchez P A 1982 Phosphate rock dissolution and availability in Cerrado soils as affected by phosphorus sorption capacity. *Soil Sci. Soc. Am. J.* 46, 339–345.
- Syers J K and Mackay A D 1986 Reactions of Sechura phosphate rock and single superphosphate in soil. *Soil Sci. Soc. Am. J.* 50, 480–485.
- Tucker D P H, Alva A K, Jackson L K and Wheaton T A (Ed) 1995 Nutrition of Florida Citrus Trees. SP 169, University of Florida, Gainesville, FL.
- 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.
- 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 seeding root elongation. *Plant Soil* 21, 21–30.
- Zapata F and Zaharah A R 2002 Phosphorus availability from phosphate rock and sewage sludge as influence by the addition of water soluble phosphate fertilizer. *Nutri. Cycl. Agroecosys.* 63, 43–48.

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