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Aggregate Size Effects on the Sorption and Release of Phosphorus in an Ultisol

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ABSTRACT

Despite extensive research on soil–P reactions, little is known of the effect of soil aggregation on these processes. This study was conducted to determine the role of aggregate size on the sorption and release of P in a Haiku clay (Typic Palehumult). A range of aggregate sizes up to 4 mm in diameter were used in this study. Autoradiography of sorbed ^{32}P and P sorption studies indicated that added P was initially sorbed to a 0.188-mm layer around aggregates and remained in this peripheral layer for up to 28 d. We defined this layer as the *reactive mass*. Analysis of P in aggregates from a 4-yr P management field experiment on the same soil indicated that diffusion of P from this peripheral layer into the aggregate was slow, requiring >2 yr for aggregate P to reach equilibrium. When P was added to a combined mix of aggregate size fractions, P sorption increased from 55 to 245 mg P kg^{-1} as mean aggregate diameter decreased from 3.4 to 0.375 mm, and was linearly related to the aggregates' reactive mass (r^2 = 0.96). Similarly, the reactive mass of aggregates was linearly correlated to P release from aggregates (r^2 = 0.99) and to the linear buffer coefficients derived from P-sorption isotherms (r^2 = 0.98). Since aggregate size is related to P sorption, soil buffering capacity, and P release from soil, it is likely that aggregation affects short- and long-term plant P availability. The effect of aggregate size, however, needs to be investigated for other soils.

PHOSPHORUS is a major limiting nutrient in many tropical soils. Many of these soils are highly aggregated due to the prevalence of low-activity clays that do not shrink and swell, high levels of Fe and Al oxides (Uehara and Gillman, 1981), and, in some cases, high organic matter contents (Perez-Escolar and Lopez, 1968). The influence of aggregation on P availability has not been examined.

Diffusion of P within aggregates is very slow. Nye and Stauton (1994) estimated the intraaggregate P diffusion coefficient of a sandy soil to be 1.5×10^{-12} cm^2 s^{-1}. This is in contrast to an average soil P diffusion coefficient of 1×10^{-8} to 10^{-11} cm^2 s^{-1} (Barber, 1984). In an aggregated soil, solute movement is primarily through interaggregate pores. Solute transport in and out of aggregates occurs primarily by diffusion because water within aggregates is immobile (Fong and Mulkey, 1990).

Gunary et al. (1964) found that added P was initially sorbed on the periphery of synthetic aggregates. Subsequent equilibration of P within large aggregates could theoretically take many years due to slow diffusion rates. For instance, the average linear diffusive movement (L) with time (t) can be estimated by: $L = (2Dt)^{1/2}$, where D is the diffusion coefficient (Barber, 1984). Using Nye and Stauton's (1994) estimate of D, the diffusive movement of P in 1 yr would be at most 0.1 mm. Consequently, P diffusion from within aggregates to aggregate surfaces in contact with the bulk soil solution may be too slow to meet plant requirements.

While soil aggregation may slow the sorption reaction and subsequent equilibration in laboratory studies (Fox and Kamprath, 1970; Munns and Fox, 1976), the relationship between P sorption and aggregate size has not been quantified. Understanding this relationship may improve predictions of P availability in soils. The objectives of this study were to determine (i) the physical distribution of recently applied P within and among soil aggregates, (ii) the effect of P distribution within aggregates on soil buffering capacity, and (iii) the effect of aggregate size on P release from soil.

MATERIALS AND METHODS

Soil Collection and Aggregate Fractionation

A 4-yr P management experiment on a Hawaiian Ultisol (clayey, oxidic, isohyperthermic Typic Palehumult) was initiated in the fall of 1988 (Cassman et al., 1993; Linquist et al., 1996). The experiment consisted of two treatments with four replications: (i) a control that never received P (0P), and (ii) a high-P treatment (+P). The +P treatment received a net cumulative input of 930 kg P ha^{-1} during the first 2 yr. The P source, triple superphosphate, was broadcast and incorporated approximately 2 mo before sowing each crop. The residual benefit of added P was measured during the next 2 yr. Four soybean (*Glycine max* [L.] Merr. cv. Clark) crops were grown between the fall of 1988 and the summer of 1990, and four additional crops (soybean and maize [*Zea mays* L.]) were grown in the 2-yr period following the last P application. The soil samples (0–25 cm) used in this study were collected at the end of the 4-yr study in the summer of 1992.

Soil samples (0–25 cm) from each plot were passed through a 4-mm sieve and then air dried. Replicate soil samples from each P treatment were combined and then separated into nine aggregate size fractions using the wet sieving method described by Elliot (1986). The fractions were: <0.053, 0.053 to 0.09, 0.09 to 0.15, 0.15 to 0.25, 0.25 to 0.5, 0.5 to 1.0, 1.0 to 2.0, 2.0 to 2.8, and 2.8 to 4.0 mm. The corresponding MAD for each fraction was <0.027, 0.072, 0.12, 0.2, 0.375, 0.75,

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Abbreviations: LSD, least significant difference; MAD, mean aggregate diameter; Pi, inorganic P; Po, organic P; SD, standard deviation.

1.5, 2.4, and 3.4 mm. The MAD will be used to identify each fraction.

Characterization of Aggregate Fractions

Analyses were performed on replicate samples of each aggregate fraction from the 0P and +P field treatments to determine total C, Pi and Po pools, and particle size. Total C was determined using a Leco CHN-600 analyzer (Leco Corp., St. Joseph, MI) after pulverizing to pass a 0.15-mm sieve. A modification of the Hedley et al. (1982) sequential P fractionation procedure was used to measure Pi and Po. We measured 0.5 *M* $NaHCO_3$- and 0.1 *M* NaOH-extractable Pi and Po and residual P. Organic P in each extract was determined as the difference between total P and Pi. Total P was measured after digesting an aliquot in H_2SO_4 and ammonium persulfate for 90 min in an autoclave (U.S. Environmental Protection Agency, 1971). Further analysis of the residual P pool in this soil indicated that at least 80%, and possibly up to 98%, of the P in this pool was inorganic (Linquist, 1995). Therefore, total Pi for each aggregate fraction was estimated as the sum of $NaHCO_3$-Pi, NaOH-Pi, and residual P. Sand and clay content were determined using the hydrometer method (Gee and Bauder, 1986).

Clay mineralogy was characterized for each aggregate fraction from the 0P field treatment by x-ray diffraction (Jones and Malik, 1994). Mineralogical analysis of the x-ray diffraction pattern was quantified using the SIROQUANT computer program (Sietronics, Pty. Ltd., 1983).

Phosphorus-32 Autoradiographs

The physical distribution of recently sorbed P in aggregates was determined using autoradiography (Gunary et al., 1964). One gram of 3.4-mm aggregates from the 0P field treatment was slowly brought to saturation with 0.01 *M* $CaCl_2$ and was then placed in a petri dish containing 30 mL of 0.01 *M* $CaCl_2$ and 186 μg P labeled with 1.85 MBq ^{32}P. After agitation on an orbital shaker (50 rpm) for 3, 14, or 28 d at room temperature, aggregates were removed, placed on filter paper to remove the free solution, and air dried. Aggregates from each agitation period were placed in separate molds containing melted paraffin wax. After the wax solidified, 0.5-mm thin sections of the aggregates were cut using a microtome. Thin sections were placed between two layers of cellophane, placed on x-ray film (Fuji RX), and transferred to film canisters for 6 min.

Preserving Aggregate Structure

In the following experiments it was imperative to maintain aggregate structure during incubation. Air-dry aggregates rupture when they come into rapid contact with free liquid. To prevent aggregate disruption, aggregates were slowly moistened by adding the desired amount of air-dry aggregates to a petri dish and placing the dish in a closed chamber with a humidifier for 2 h. This raised the moisture content of aggregates to approximately 0.13 kg H_2O kg^{-1} and minimized their disruption when rapidly introduced to a liquid solution.

Adequate agitation of solution around the aggregates during incubation was achieved by placing petri dishes containing the aggregates and solutions on an orbital shaker at 50 rpm. Shaking aggregates in solution or swirling the aggregates more vigorously on an orbital shaker destroyed the aggregates.

Phosphorus Sorption by Different Aggregate Size Fractions

One gram from each of seven aggregate fractions (0.12, 0.2, 0.375, 0.75, 1.5, 2.4, and 3.4 mm) from the 0P field treatment was placed in a 10-cm-diam. plastic petri dish and slowly wetted as described above. The aggregate samples were then treated with 30 mL of 0.01 *M* $CaCl_2$ containing 0 (control) or 186 μg P as $Ca(H_2PO_4)_2 \cdot H_2O$ (+P). Duplicate samples were incubated at room temperature for 1, 7, 30, or 100 d. Following incubation, the solution was decanted, and aggregates were air dried. Aggregates were separated to the original size fractions by dry sieving. Aggregate recovery, determined by weighing each fraction after dry sieving and comparing it to the initial weight, exceeded 95%. Total P was estimated on a 0.5-g sample, which had been pulverized to pass a 0.15-mm sieve, by digestion in H_2SO_4 and H_2O_2 (375°C) for 5 h (Tiessen and Moir, 1993). Total P sorbed by each aggregate fraction for each incubation period was calculated as the difference between the control and the +P treatment.

Phosphorus Release from Aggregate Fractions

Ten grams of the 2.4-, 1.5-, 0.75-, 0.375-, and 0.2-mm aggregates from the 0P treatment (the quantity of 3.4-mm aggregates was insufficient for this experiment) were slowly wetted as described above and then transferred to a 10-mL syringe containing 0.01 *M* $CaCl_2$ and packed at both ends with glass wool. Fresh Mehlich-1 extractant (0.05 *M* HCl and 0.0125 *M* H_2SO_4) was continuously pumped through the aggregates at a rate of 1 mL min^{-1}, providing about one macropore volume of extractant every 5 min. Samples of solution were collected periodically during a 56-h period. The samples were filtered through a 0.45-μm membrane filter and were then analyzed for P using the method of Murphy and Riley (1962). Phosphate release from aggregates <0.2 mm could not be determined due to preferential flow of the extractant through soil pore channels (channeling).

Aggregate Size Effects on Soil Buffering Capacity

Phosphorus sorption isotherms were determined for six aggregate size fractions from the 0P treatment: 3.4, 2.4, 1.5, 0.75, 0.375, and 0.2 mm. Isotherms were also determined for a sample of the 2.4-mm aggregates that had been pulverized to pass a 0.15-mm sieve ("2.4 pulv") and an unground whole soil sample that had not been separated by aggregate fractionation ("natural"). One gram of each sample was added to separate petri dishes. This weight of material formed a single layer on the bottom of the dish, thus uniformly exposing the outer surfaces of both large and small aggregates to the bulk solution. The samples were treated with 30 mL of 0.01 *M* $CaCl_2$ containing $Ca(H_2PO_4)_2 \cdot H_2O$, such that P was applied at a rate of 0, 42, 84, 168, or 336 mg P kg^{-1}. Treatments were replicated twice. The soil solution mixture was agitated gently (rotary shaker, 50 rpm) at room temperature for 6 d. Following incubation, the solution was analyzed for P (Murphy and Riley, 1962). Adsorbed P was calculated as the difference between the amount of P added and the P remaining in solution.

A separate isotherm was determined for a whole soil sample that had not been separated by aggregate fractionation to determine the effect of vigorous shaking on the soil buffering capacity ("shake"). The P rates and the soil/solution ratio were the same as described above, except the procedure was done in 40-mL centrifuge tubes instead of petri dishes. The tubes containing the soil were placed on a reciprocal shaker (180 rpm) for 30 min twice daily for 6 d. This method is the same as that of Fox and Kamprath (1970) except for using a soil/solution ratio of 1:30 instead of 1:10.

Table 1. Properties of aggregate size fractions of the Haiku clay.

Mean aggregate diameter	Organic P†					Soil in aggregate fraction
	$NaHCO_3$	NaOH	C	Clay	Sand	
mm	mg kg^{-1}		g kg^{-1}			%
3.4	27.4	272	27.6	615	49	12
2.4	28.4	270	27.4	613	50	15
1.5	29.2	268	27.1	617	60	24
0.75	28.7	272	27.3	615	51	21
0.375	29.0	278	27.5	616	40	16
0.20	28.9	276	27.6	610	37	7
0.12	29.0	272	27.3	617	51	3
0.072	26.8	261	26.8	592	90	1
0.027	22.9	230	24.4	NA‡	NA	1
Pooled SD	2.6	19	0.7	8	7	2

† Determined by a modification of the Hedley et al. (1982) procedure.
‡ NA = not available.

Statistical Analysis

The relationship between sorbed P and aggregate size was fit to a linear function for each incubation period (1, 7, 30, and 100 d). The homogeneity of the regression coefficients was tested (Gomez and Gomez, 1984) to determine the effect of time on the distribution of sorbed P in different aggregate fractions. Similarly, the homogeneity of linear regression coefficients relating extractable P to extraction time for each aggregate size was tested to analyze the effect of aggregate size on P release. Differences among means were tested by calculating LSD values at the 0.05 level.

RESULTS AND DISCUSSION

Aggregate Characterization

Fifty-one percent of the Haiku clay consisted of aggregates exceeding 1.0 mm in diameter (Table 1). These results are similar to those of Grohmann (1960), who found that 61 and 47% of aggregates in a cultivated Brazilian Oxisol and Ultisol, respectively, exceeded 1 mm in diameter. Tropical soils often have a large proportion of water-stable aggregates due to a high content of Fe and Al oxides (Uehara and Gillman, 1981). The soil used in our study also had a relatively high C content, averaging 26.6 g kg^{-1} (Table 1), which may have promoted aggregation (Perez-Escolar and Lopez, 1968).

Total C, $NaHCO_3$-Po, and NaOH-Po did not differ between the 0P and +P field treatments; therefore, the results were combined (Table 1). All aggregate size fractions except the two smallest fractions (<0.027 and 0.072 mm) had similar amounts of $NaHCO_3$-Po, NaOH-Po, and total C, and similar particle-size distribution and clay mineralogy (Tables 1 and 2). The two smallest fractions, which represented only 2% of the soil mass, tended to have lower extractable Po, C, clay, and goethite than the larger fractions. Organic P extracted by $NaHCO_3$ and NaOH averaged 28 and 266 mg kg^{-1}, respectively. Clay and sand averaged 612 and 54 g kg^{-1}, respectively. Goethite, gibbsite, and kaolin are minerals with substantial P sorption capacity (Table 2). Of these, goethite, which averaged 210 g kg^{-1} clay, has the highest P sorption capacity (Jones, 1981; Parfitt, 1989).

Table 2. Clay mineralogy of different aggregate size fractions from the Haiku clay.

MAD†	Goethite	Anatase	Hematite	Quartz	Kaolin	Illite	Gibbsite	Other‡
mm	g kg^{-1}							
3.4	217	114	64	163	76	328	29	14
2.4	247	69	67	162	89	310	38	17
1.5	206	101	58	139	84	361	35	16
0.75	208	102	59	129	85	364	32	20
0.375	206	84	58	154	84	361	32	20
0.20	216	110	54	153	78	337	30	22
0.12	222	85	56	133	80	345	49	30
0.072	158	79	55	128	79	436	30	37

† Mean aggregate diameter.
‡ Interstratified illite and smectite.

Distribution of Applied Phosphorus in Aggregates

Phosphorus was initially sorbed and remained on the periphery of 3.4-mm aggregates following 28 d of incubation in ^{32}P solution (Fig. 1). Gunary et al. (1964) and Willet et al. (1988) also found that P was initially sorbed to the surface of ferrihydrite particles and synthetic aggregates coated with amorphous Fe.

Since P is sorbed on the periphery of aggregates, smaller aggregates should initially sorb more P than larger aggregates due to the greater surface area per unit mass of smaller aggregates. Figure 2A shows the relationship between P sorption and aggregate size after P was added to a combined mix of different aggregate size fractions. Phosphorus sorption by each fraction 1 and 7 d after P addition was the same, so results were combined for presentation (1&7 d). Phosphorus sorption increased from 55 to 245 mg P kg^{-1} as aggregate size decreased from 3.4 to 0.375 mm. Sorption did not continue to increase as aggregate size decreased below 0.375 mm.

The surface area of aggregates alone did not account for the differences in P sorption between aggregate sizes; otherwise, P sorption would continue to increase as aggregate size decreased below 0.375 mm. Since P sorption did not increase in aggregate sizes <0.375 mm, we suggest that P was initially sorbed to a depth of 0.188 mm (the mean radius for 0.375-mm-diam. aggregates) around the periphery of aggregates. The depth of ^{32}P sorption in aggregates is consistent with this depth (Fig.

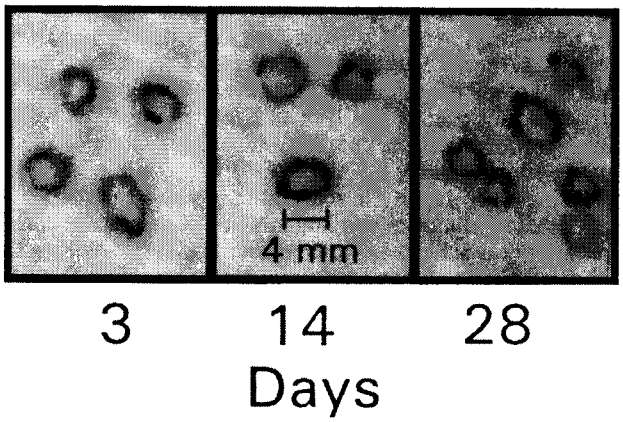


Fig. 1. Autoradiographs of aggregate (3.4-mm fraction) cross-sections exposed to ^{32}P-labeled solution for 3, 14, and 28 d.

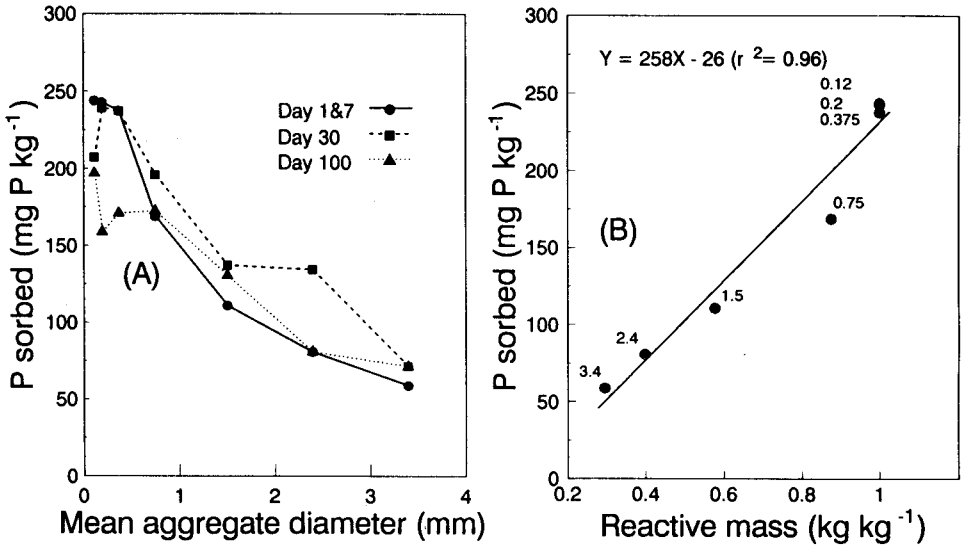


Fig. 2. (A) Phosphorus sorbed (total P in +P minus total P in control) by each aggregate fraction after exposure to a common P solution containing 186 mg P kg^{-1} soil (+P) or no P (control) for 1, 7, 30, or 100 d (data for Days 1 and 7 were similar and were combined for presentation); (B) P sorbed at Days 1 and 7 as a function of reactive mass (the mean aggregate diameter is beside each point). The LSD(0.05) is 54 mg P kg^{-1} and is for comparison of P sorbed by each fraction at different times.

1). We define the mass of soil in this outer 0.188-mm layer of aggregate as the *reactive mass*.

Assuming aggregates approximate spheres of uniform density, the MAD was used to estimate the reactive mass of each aggregate fraction (Table 3). Aggregates ≤0.375 mm in diameter consisted entirely of reactive mass, while the 3.4-mm aggregates had only 30% reactive mass. Initial (1&7 d) P sorption as a function of reactive mass was linear and highly significant (Fig. 2B).

We hypothesize that equilibration following P addition will occur through redistribution of P by diffusion from smaller, P-rich aggregates, to larger aggregates with lower P content. The P sorption by each aggregate fraction should be similar at equilibrium because the mineralogy and clay content of each fraction were comparable (Tables 1 and 2). Testing for homogeneity among regression coefficients derived in relating P sorption to MAD indicated no significant change in P distribution among aggregates during the 100-d incubation period (Fig. 2A). This suggests that a longer incubation period would be needed to measure the slow changes due to P diffusion in this soil.

Phosphorus Release from Different Aggregate Size Fractions

After P is sorbed to soil surfaces, P availability to plants is determined by the desorption rate. The rate of P release from different aggregate size fractions was measured using a continuous-flow system and Mehlich-1 extractant (Fig. 3A). The rate of P extraction was essentially linear with time to 56 h, and inversely proportional to aggregate size. The rate of P extraction, based on the linear coefficient (Fig. 3A) from the 0.2-mm fraction, was double that of the 2.4-mm fraction.

Table 3. Reactive mass of various aggregate fractions (kilograms reactive mass per kilogram total aggregate mass). Values are the mass of aggregates to a depth of 0.188 mm.

Aggregate diameter	Mean diameter	Reactive mass
mm		kg kg^{-1}
2.8–4.0	3.4	0.296
2.0–2.8	2.4	0.399
1.0–2.0	1.5	0.578
0.5–1.0	0.75	0.875
<0.25–0.5	<0.375	1.0

The relationship between cumulative P extracted after 56 h and reactive mass was linear and highly significant (Fig. 3B). Similarly, slope coefficients (Fig. 3A) were linearly related to reactive mass (r^2 = 0.99) (data not shown). Unlike the sorption studies, where P sorption did not increase in aggregate fractions with MAD ≤0.375 mm (Fig. 2A), P release was significantly greater (based on testing the homogeneity of regression coefficients) from 0.2-mm than from 0.375-mm aggregates (Fig. 3A). This observation indicates that the depth of the reactive mass layer that governs P release from aggregates may be smaller than for sorption. The aggregate size below which P release would not continue to increase, however, could not be determined using our methodology due to channeling when aggregate size was too small; therefore, the reactive mass derived from sorption studies (Table 3) was used.

Horn and Taubner (1989) found that K release from large aggregates was slower than from small aggregates due to a longer diffusion path length. Diffusion rates are much lower for P than for K (Barber, 1984). Our results suggest that P inside large aggregates was not rapidly released into solution since short-term release of P from aggregates was closely related to the reactive mass on the periphery of aggregates (Fig. 3B). Thus, P inside large aggregates of this soil may not be immediately available to plants.

Phosphorus uptake declined by 34% 2 yr following a cumulative 930 kg P ha^{-1} addition to this soil (Linquist et al., 1996). This decline in P availability could not be

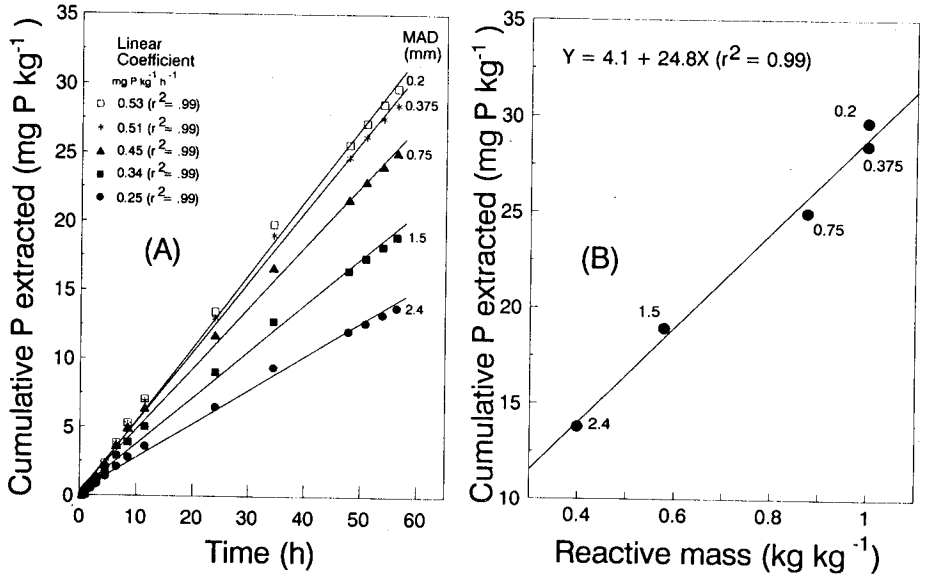


Fig. 3. Cumulative P recovered after continuous extraction (A) from different aggregate size fractions (all slope coefficients differed significantly at the 0.05 level); (B) for 56 h as a function of reactive mass (the mean aggregate diameter is beside each point).

explained by a conversion of P to less labile forms (Linquist, 1995). Nye and Stauton (1994) suggested that slow diffusion of P into aggregates probably accounts for the slow continual reactions of P with soil observed in many lab experiments, based on studies of P diffusion in microaggregates (<0.212 mm in diameter). Our results on larger aggregates support their hypothesis. We further suggest that diffusion of P into the interior of aggregates may be the cause of the declining plant P availability observed in this field study.

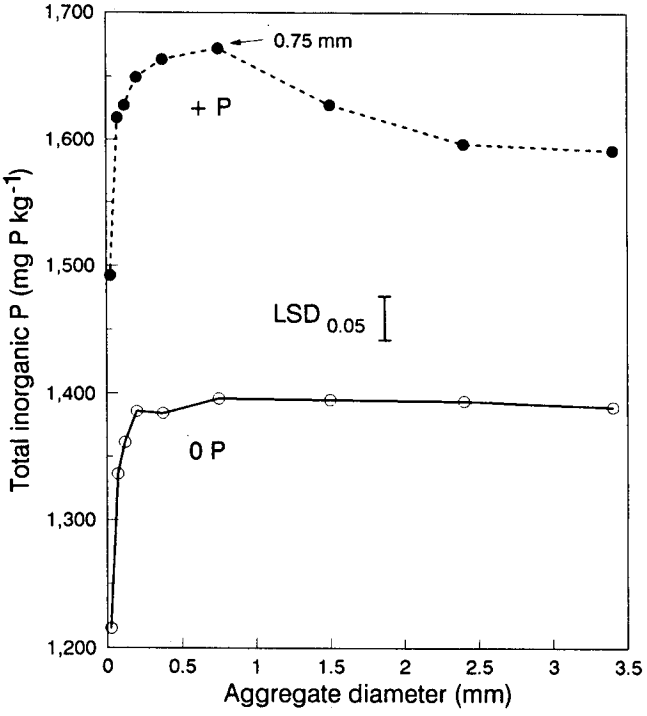


Fig. 4. Total inorganic P as a function of mean aggregate diameter 2 yr following a cumulative P application of 0 (0P) and 930 kg P ha^{-1} (+P). The LSD is for comparison of P in different aggregate size fractions within the same P treatment.

Phosphorus Content of Aggregates from Field Soil after Fertilization

To verify the effects of aggregate size on P sorption and release in the field, the P contents of different aggregate size fractions from the 0P and +P field treatments were measured. Total Pi in the +P treatment aggregates increased from 1590 to 1672 mg P kg^{-1} as aggregate size decreased from 3.4 to 0.75 mm (Fig. 4). These results are similar to data presented in Fig. 2A, where smaller aggregates, with greater reactive mass, sorbed more P than larger aggregates. This soil was sampled 2 yr after the last P application. The persistent difference in P content among the larger aggregates demonstrates the extremely slow nature of the equilibration process.

Total Pi content of aggregates from both +P and 0P treatments decreased as MAD decreased below 0.75 mm (Fig. 4). Based on results presented in Fig. 2B, the smaller aggregate fractions would have initially sorbed more P when it was applied. Where P is removed by plant uptake, small aggregates will become relatively more depleted than large aggregates since the rate of release from small aggregates is greater than from large aggregates (Fig. 3). The low Pi content of the two smallest aggregate fractions is probably due to a combination of plant uptake and lower clay and goethite contents (Tables 1 and 2).

Aggregate Size Effects on Buffering Capacity

Phosphate sorption isotherms are commonly used to measure soil P-buffering capacity. Buffering capacity (slope of the regression curve, Barber, 1984) was inversely related to aggregate size between 3.4 and 0.75 mm (Fig. 5). Soils with an aggregate size $\leq$0.375 mm due to sieving, grinding ("2.4 pulv"), or vigorous shaking ("shake") had the highest buffering capacity.

Sorption isotherm data were fit to the quadratic equation:

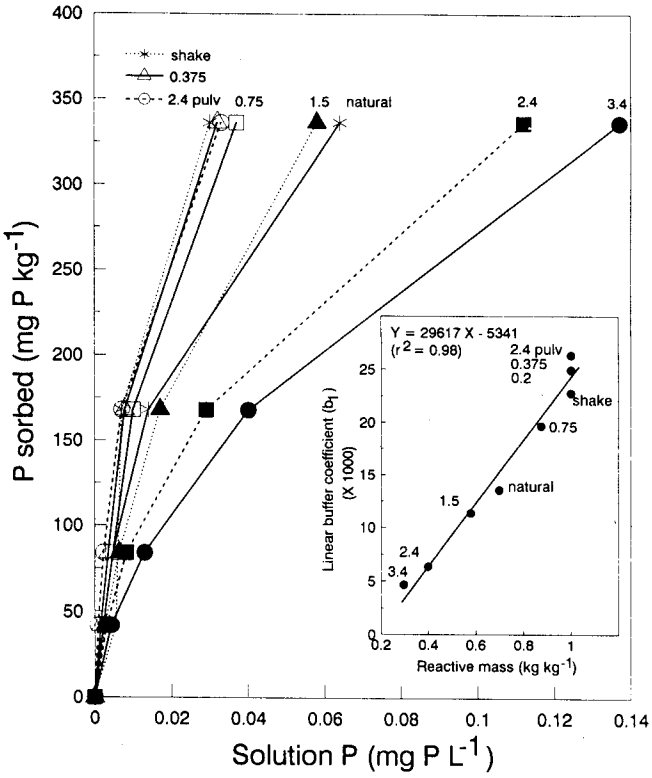


Fig. 5. Phosphorus sorption isotherms of five aggregate size fractions, a pulverized 2.4-mm sample (2.4 pulv), an unfractionated soil sample (natural), and an unfractionated soil sample in which the aggregates were destroyed by vigorous shaking during the incubation period (shake). Insert: Regression of linear buffer coefficients (b_1) vs. reactive mass.

$$\text{P sorbed} = b_1(\text{solution P}) + b_2(\text{solution P})^2$$

Coefficients of determination (r^2) for these regressions exceeded 0.997. The linear buffer coefficient (b_1), which explained >90% of the variation in the amount of P sorbed, was regressed against reactive mass. The fit was linear and highly significant (Fig. 5, insert), suggesting that aggregate size had a large influence on soil P buffering capacity. The reactive mass for the "natural" soil was calculated based on the aggregate size distribution of this soil (Table 1). The reactive mass for the vigorously shaken soil ("shake") was assumed to be 1.0 kg kg^{-1} since shaking destroyed the aggregates.

Our results indicate that standard P sorption isotherm methods, which grind and vigorously shake the soil (e.g., Fox and Kamprath, 1970), probably expose diffusion-limited P sorption sites, overestimating the buffering capacity of field soil. For example, to attain a solution P value of 0.03 mg P L^{-1}, 100 mg kg^{-1} more P needed to be added to the vigorously shaken soil ("shake") than to the undisturbed ("natural") soil (Fig. 5). Cassman et al. (1981) estimated that the recommended P application rate for optimal yields on this soil was >500 kg P ha^{-1}. Their estimate was based on P sorption isotherms where the soil was vigorously shaken and aggregates destroyed (Fox and Kamprath, 1970). Despite these high recommendations, Cassman et al. (1993) found that 100% of maximum yield was achieved by applying 100 kg P ha^{-1} to this aggregated soil.

Clay content is highly correlated with soil buffering capacity due to high specific surface area (Cox, 1994). However, fertilizer recommendations based on clay content as proposed by Lins et al. (1985) will not necessarily be precise across a range of soil types. Precision will be lost if aggregate size distribution varies widely, since reactive clay surfaces may be occluded within aggregates.

SUMMARY AND CONCLUSIONS

Tropical soils are often P deficient as well as highly aggregated. Availability of applied P depends, to a large degree, on the sorption and subsequent release of P from soil surfaces. The purpose of this investigation was to determine the effect of aggregation on these processes. Our results indicate that applied P is initially sorbed on the periphery of aggregates. Subsequent physical movement of P by diffusion into or out of aggregates is an extremely slow process, requiring years to reach equilibrium.

The potential implications of these findings for improving short- and long-term P management strategies and refining soil P tests are significant. We speculate that recently applied P will be more plant available in soils with a high proportion of large aggregates due to lower reactive mass and, thus, lower P buffering capacity. With time, P diffuses into aggregates and becomes less available for immediate plant uptake; therefore, long-term residual P benefits would be expected to be lower in soils with a high proportion of large aggregates.

Current soil test methodology for estimating available P in soils generally requires shaking soil in an extractant that destroys aggregates. These procedures extract labile P from throughout the aggregate, giving a potentially erroneous value of available P since some of this P may be unavailable to plants due to its physical location within aggregates. Our results indicate that plant-available P is on the periphery of aggregates; therefore, indices of availability should measure labile P on the outer surface of aggregates. Developing soil tests where the aggregates remain intact during the extraction or where the soil aggregate size distribution is accounted for may lead to estimates of available P that could be applied across a wider range of soils.

We have only reported on how aggregate size affects P sorption and release in one soil. Further assessment is needed to determine whether these results are of significance in other soils that differ in mineralogy and P-sorption capacity.

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