

# Soil Aggregate Size Affects Phosphorus Desorption from Highly Weathered Soils and Plant Growth

X. Wang, R. S. Yost,\* and B. A. Linquist

## ABSTRACT

Because plant absorption of P depends on the desorption of P from soil, understanding P desorption from soils may improve the precision of P diagnosis and fertilization recommendations. Many soils with high P retention due to high levels of Fe and Al are also highly aggregated. Extractable P is sometimes higher on larger size aggregates, which will probably result in increased P release from aggregates. The effects of aggregate size on P availability of three highly weathered soils were quantified with a column-leaching study and a pot experiment. Phosphorus desorption by leaching from small aggregates was greater than that from large aggregates when P had been added to the bulk soil (Kapaa and Leilehua soils) and a mixture of different-sized aggregates (Leilehua soil). When aggregates were separated and then P added, however, P desorption was greater from large aggregates (4–6 mm) than from small aggregates (<0.5 mm). Conformity of the P desorption data to the parabolic diffusion and expanded Elovich equations suggests that P desorption is probably controlled by diffusion processes. A pot experiment showed that total P in lettuce (*Lactuca sativa* L.) and soybean [*Glycine max* (L.) Merr.] shoots, and the root dry weights of plants grown in the large aggregates (2–6 mm) were higher than for plants grown in the small aggregates (<0.5 mm) after equal amounts of P were added to the separated aggregate fractions. Increased P uptake with increased aggregate size was attributed to increased P release from aggregates because of reduced P fixation. The results suggest that soil management that favors soil aggregation may, in some cases, increase availability of applied P. Perhaps the distribution of soil aggregates should be considered in making P management decisions.

ACCURATE ASSESSMENT of P availability in soils is becoming increasingly important from perspectives of sustainability of agriculture and protecting the environment. Although influences of soil chemical properties on P release from soils and uptake by plants are well documented, prediction of P requirements remains imprecise (Chen et al., 1997). For example, Cassman et al. (1993) found that the application of 100 kg P ha<sup>-1</sup> to an Ultisol produced the maximum yield of soybean, although the recommended P application rate, based on the Fox and Kamprath method (Fox and Kamprath, 1970), was more than 500 kg P ha<sup>-1</sup> (Cassman et al., 1981). One possible solution to such imprecision is a better understanding of the processes controlling P sorption and desorption from soils, particularly high P sorbing soils. Evidence shows that soil aggregate size influences P sorption and bioavailability (Wiersum, 1962; Gunary et al., 1964; Cornforth, 1968; Misra et al., 1988; Linquist et al., 1997). Nutrient uptake from small aggregates often is greater than that from large aggregates

(Wiersum, 1962; Cornforth, 1968; Misra et al., 1988), but freshly applied P may penetrate only a thin layer around soil aggregates (Gunary et al., 1964; Linquist et al., 1997), suggesting that larger soil aggregates with relatively less surface area than small aggregates may reduce P fixation and result in increased availability of recently applied P. With equivalent levels of extractable P, one might expect that desorption from larger aggregates may be lower if P diffuses deeply into the aggregates.

Soil P release may affect both P supply to plants and P discharge from watersheds. Desorption of P would, therefore, probably be more pertinent than P sorption when evaluating plant-available P and P buffering properties of soil, an observation noted many years ago by Fox and Kamprath (1970). Several experimental techniques have been used to investigate P desorption. These include extraction of soil P with P-free solution (Kafkafi et al., 1967; Barrow, 1983), addition of materials with high capacities to bind P in order to deplete P in soils (Amer et al., 1955; Yang and Skogley, 1992), and leaching of soil columns with P-free solutions (Sawhney, 1977; van der Zee and Gjaltema, 1992). The soil column leaching method was used in our experiments because it prevented the breakup of soil aggregates resulting from the vigorous shaking required by the other methods. Leaching soil columns also permitted the removal of desorbed P with time, which simulates nutrient removal by plant uptake more closely than batch equilibration.

The objectives of this study were (i) to investigate the effect of aggregate size on P availability as measured by extractable P and P desorption from different soils and (ii) to test the hypothesis that increased aggregation increases P uptake by plants through decreased sorption of applied P.

## MATERIALS AND METHODS

### Soils

Two Oxisols (Kapaa and Wahiawa series) and an Ultisol (Leilehua series) from Hawaii were selected for this study. Selected properties of the soils and P rate for each soil are presented in Table 1.

Eight aggregate-size fractions were obtained from the Wahiawa and Kapaa soils by dry-sieving to obtain sizes of < 0.053, 0.053 to 0.125, 0.125 to 0.25, 0.25 to 0.5, 0.5 to 1, 1 to 2, 2 to 4, and 4 to 6 mm. The target P concentrations (1.6 mg P L<sup>-1</sup>) in solution for the Wahiawa and Kapaa soils were maintained from 1971 to 1989 (Rajbhandari, 1991), and 0.5 M NaHCO<sub>3</sub>-extractable P in these soils was very high (Table 1). For the

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**Abbreviations:** Delta P, difference in extractable P between before planting and after planting; GMD, geometric mean diameter; SE, standard error.

**Table 1. Selected properties of three highly weathered soils from Hawaii.**

Soil series	Classification	pH	OC	Clay	P treatment	Solution P	Olsen P	GMD†
			— g kg <sup>-1</sup> —		mg P kg <sup>-1</sup>	mg P L <sup>-1</sup>	mg P kg <sup>-1</sup>	
Kapaa	Very fine, sesquic, isohyperthermic, Anionic Acrudox	5.5	71	500	NA‡	1.6§	204	1.253
Wahiawa	Very fine, kaolinitic, isohyperthermic, Rhodic Eutruxox	5.9	24	910	NA	1.6§	283	0.655
Leilehua	Clayey, oxidic, isohyperthermic, Typic Kandihumult	4.5	57	790	800¶	NA	198	0.988

† GMD is the geometric mean diameter of aggregates (mm).

‡ NA is not applicable.

§ Solution P concentration attained using the P sorption isotherm curve (Fox and Kamprath, 1970).

¶ The mixture of differing aggregate fractions was incubated with added P of 800 mg kg<sup>-1</sup> soil for 180 d.

Leilehua soil, replicated mixtures of equal amounts of five aggregate fractions (<0.5, 0.5–1, 1–2, 2–4, and 4–6 mm) were enriched with 800 mg P kg<sup>-1</sup> [Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub> · H<sub>2</sub>O] due to very low extractable P content (no P fertilization was recorded when the sample was taken), and equilibrated in plastic bags. The mixtures were exposed to air and put through wetting and drying cycles for 180 d at 25 ± 2°C. The soil samples were rewetted to the estimated field capacity with deionized water when the samples had dried. Then, the mixture was separated into the original size aggregates and changes in aggregate distribution were measured. Phosphorus in different aggregate fractions and bulk soils was extracted with 0.5 M NaHCO<sub>3</sub> (Olsen et al., 1954) and determined with the ammonium molybdate reagent with ascorbic acid according to the Watanabe and Olsen (1965) modification of the Murphy and Riley (1962) procedures.

### Phosphorus Desorption

The influence of aggregate size on P desorption was determined by leaching soil columns containing the various-sized aggregates. Aggregate fractions were <0.5, 1 to 2, 4 to 6 mm, and sieved bulk soil for the Leilehua soil. The bulk soil was sieved through a 2-mm screen such that aggregates larger than 2 mm were destroyed. Hereafter the bulk soil refers to the 2-mm sieved soil as described above. The aggregate fractions were 0.053 to 0.125, 0.5 to 1, 4 to 6 mm, and bulk soil for the Wahiawa soil and 0.125 to 0.25, 1 to 2, 4 to 6 mm, and bulk soil for the Kapaa soil. A preliminary experiment showed that P desorption from the 10-g soil column was not significantly different from a 50-g soil column at a probability level of 0.05 (data not shown). Thus, 10 g of each sample were uniformly packed into a 20-mL syringe with acid-washed quartz sand at both ends. Whatman no. 42 filter paper was used to separate the soil in the column from the sand. The soil columns were then saturated with 0.001 M CaCl<sub>2</sub> from the bottom in a vacuum. A constant solution flux of 0.001 M CaCl<sub>2</sub> through the vertical column was maintained with a peristaltic pump. The leachate rate was maintained at 2.3 × 10<sup>-5</sup> m s<sup>-1</sup> (or 7.2 × 10<sup>-5</sup> mL s<sup>-1</sup>). The leachate was collected at 25-min intervals for 2 to 6 wk and solution P was determined by the phosphomolybdate method (Watanabe and Olsen, 1965). Cumulative desorbed P was then calculated from P concentration and volume of the effluent. The experiment was replicated two times. Phosphorus desorption was accomplished one soil and one replication at a time. At the same time, another sample for each treatment was used to determine 0.5 M NaHCO<sub>3</sub>-P.

In order to quantify the individual effects of aggregate size and the initial extractable P level on P desorption, P was applied at 800 mg P kg<sup>-1</sup> to each of the aggregate fractions of the Leilehua soil, and incubated for 28 d. Aggregate size fractions were <0.5, 0.5 to 1, 2 to 4, and 4 to 6 mm and contained similar levels of extractable P (1.76, 1.84, 1.52, and 1.58 mg P kg<sup>-1</sup>, respectively) prior to P addition. After incubation for 28 d, P was desorbed from the individual aggregate fractions in the columns described above.

At the completion of leaching, the samples were air-dried and separated into the original size fractions. The aggregate recoveries, the ratio of the weight of each aggregate fraction after dry sieving to the initial weight, were calculated.

### Kinetic Curves

Kinetic curves of P desorption from the soil samples were obtained by plotting the amount of cumulative desorbed P vs. pore volume, where the pore volume is the volume of water per unit area held in the wetted soil pores of the column during transport (Jury et al., 1991). One pore volume is equal to  $L\theta$  where  $L$  is the length of the soil column and  $\theta$  is the volumetric water content. The means and standard error (SE) for all samples were 4.0 ± 0.16 cm, 64.8 ± 5.7% for both  $L$  and  $\theta$ , respectively. The parabolic diffusion (Vig and Dev, 1979), power function (Kuo and Lotse, 1974), simple Elovich (Chien and Clayton, 1980), and expanded Elovich equations (Polyzopoulos et al., 1986; Raven and Hossner, 1994) were evaluated for their ability to fit P desorption data with pore volume data (Table 2). Graphical, linear, and nonlinear regression procedures with S-PLUS version 3.3 (Statistical Science, 1995) were used. Goodness of fit of the kinetic equations to the data was evaluated with the coefficient of determination ( $r^2$ ) and SE. The first- and second-order equations were not considered because preliminary graphical tests (data not shown) indicated that these equations did not adequately describe the P desorption data.

### Pot Experiment

A pot experiment was conducted in the greenhouse to determine the effect of aggregate size on P uptake by lettuce and soybean in the Leilehua soil. These two crops were selected because they have different rooting characteristics. This soil was the same as the Leilehua soil used for P desorption except the sample for P sorption was enriched with P. The experimental design was a randomized block with three replications for each crop, with five P rates (0, 62.5, 125, 250, and 500 mg P kg<sup>-1</sup> soil), three aggregate sizes (<0.5, 0.5–2, and 2–6 mm), and bulk soil passing a 2 mm sieve. The P-deficient Leilehua soil was first separated into aggregates with sizes of <0.5, 0.5 to 2, and 2 to 6 mm. The initial 0.5 M NaHCO<sub>3</sub>-extractable P in aggregate fractions ranged from 1 to 1.8 mg P kg<sup>-1</sup>. The samples were treated with 2000 mg kg<sup>-1</sup> CaCO<sub>3</sub> to raise the pH to 5.5 ± 0.1. Each fraction of aggregates and the bulk soil were then equilibrated with 0, 62.5, 125, 250, and 500 mg P kg<sup>-1</sup> soil (P applied as monobasic calcium phosphate) 4 wk before planting. After incubation, the soil samples (500 g pot<sup>-1</sup>) were mixed with vermiculite (1:1 by volume) to minimize differences in water holding capacity due to differing sized aggregates. The water content was maintained at field capacity throughout the experiment. Seeds of lettuce and soybean were directly planted in the aggregate-vermiculite mixture. The seedlings were thinned to five per pot after germination. The lettuce and soybean plants were harvested 30 and

**Table 2.** Kinetic equations that were evaluated for their ability to describe P desorption from the soils and aggregate size fractions.

Name	Equation†	Reference
Parabolic diffusion	$Q = a + b (PV)^{0.5}$	Vig and Dev (1979)
Power function	$Q = a (PV)^b$	Kuo and Lotse (1974)
Simple Elovich	$Q = a + b \ln(PV)$	Chien and Clayton (1980)
Expanded Elovich	$Q = a + b \ln(PV + c)$	Polyzopoulos et al. (1986)

†  $Q$  = amount of desorbed P at pore volume (PV);  $a$ ,  $b$ ,  $c$  = constants.

32 d after planting, respectively. The 0.5 M NaHCO<sub>3</sub>-P (Olsen et al., 1954) of each aggregate-size class after fertilization was determined before planting and after harvest. The difference in extractable P between before planting and after planting (Delta P) was calculated.

Roots that could be easily separated from soil by hand were collected and cleaned with water. Plant shoots and roots were oven-dried at 70°C and weighed. Plant shoots were ground, and duplicate samples of 0.2000 g were dry-ashed in a muffle furnace at 500°C for 4 h. The ash was dissolved in 0.1 M HCl. Phosphorus concentrations in ashed samples were determined by the phosphomolybdate method (Murphy and Riley, 1962).

### Statistical Analysis

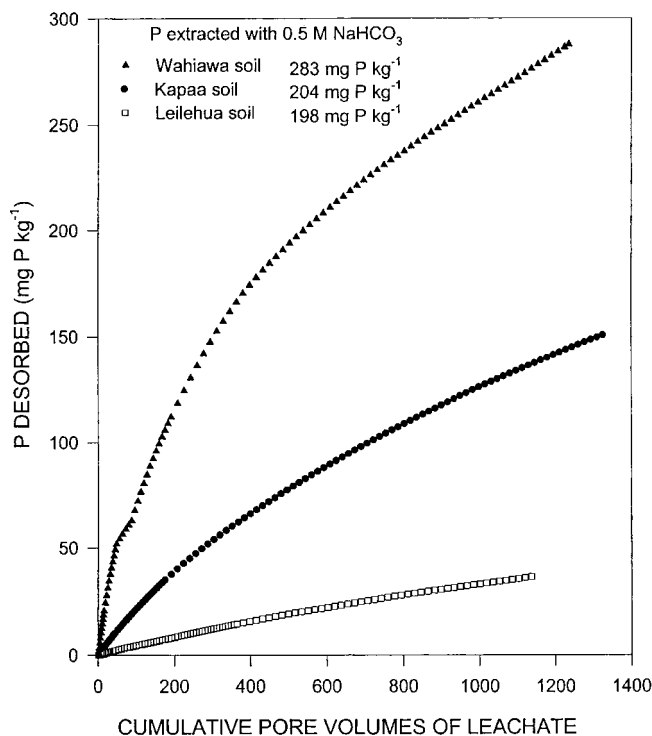
Analysis of variance tables for P uptake and dry weight of roots were constructed. Phosphorus rate and aggregate size were treated as fixed factors because of intrinsic interest in them. The adequacy of the model was evaluated by comparing a histogram of residuals, normal quantile-quantile plot (qqplot) of residuals, and scatter plot of residuals vs. fitted values. Diagnostic plots indicated no outliers or lack of homogeneity in error variances for the soybean data. However, there were nonconstant error variances and outliers for the lettuce data. The logarithmic transformation of the total P in lettuce shoots and dry weight of roots substantially improved the lack of fit at large values, as expected. No attempt was made to remove outliers in the residual plots.

The relationship between Delta P and the total P in shoots was fitted using a linear regression model.

## RESULTS AND DISCUSSION

### Phosphorus Desorption from Different Soils

Differences in P desorption among the three soils were much greater than differences in 0.5 M NaHCO<sub>3</sub>-extractable P (Fig. 1 and extractable P data inserted in Fig. 1). For example, the cumulative desorbed P at 1000 pore volumes was 25, 125, and 275 mg P kg<sup>-1</sup> for the Leilehua, Kapaa, and Wahiawa soils, respectively, while the initial 0.5 M NaHCO<sub>3</sub>-extractable P contents in the corresponding soils were 198, 204, and 283 mg P kg<sup>-1</sup>. The P concentration in 0.001 M CaCl<sub>2</sub> leachate of the Wahiawa soil was >2 mg P L<sup>-1</sup> at the beginning of leaching; in contrast, the initial P in the leachate of the Leilehua soil was <0.1 mg P L<sup>-1</sup> (data not shown). The rate of P desorption, however, decreased as P desorption proceeded for the Wahiawa soil, while the rate for the Leilehua soil showed little change with increasing pore volumes of leachate (Fig. 1). Nevertheless, the rate of desorption remained much greater from the Wahiawa soil.



**Fig. 1.** Cumulative desorbed P with increased leaching from the Wahiawa, Kapaa, and Leilehua soils. Standard errors of the expanded Elovich equation estimated at mean value were 2.58, 0.59, and 0.09 for the Wahiawa, Kapaa, and Leilehua soils, respectively.

### Phosphorus Desorption from Aggregates of Phosphorus-Fertilized Soils

After P was added to the bulk soil (Wahiawa and Kapaa) or to the mixture of differing aggregate fractions (Leilehua), the cumulative P release from small aggregates was consistently greater than from large aggregates (Fig. 2). The lower P desorption from larger aggregates may be attributed to the decreased accessibility of leaching solution to sorption sites within aggregates, increased diffusion distance, or less initial extractable P. The results may explain the observations of Wiersum (1962), Cornforth (1968), and Misra et al. (1988) that P uptake by a plant grown in soil with small aggregates was greater than by a plant grown in soil having large aggregates.

The relative differences in P release from different aggregate fractions of the Wahiawa soil were small compared with those from the Kapaa and Leilehua soils (Fig. 2). One of the reasons was the difference in extractable P among aggregate fractions. Phosphorus extracted with 0.5 M NaHCO<sub>3</sub> from the small aggregate fractions was much greater than that from the large aggregate fractions of the Kapaa and Leilehua soils, while there were almost no differences in the extractable P among aggregate fractions in the Wahiawa soil (data not shown). Another reason for differences among the soils may be related to the breakup of large aggregates during leaching, which may have increased P release from large aggregates by exposing more sorption sites inside the aggregates to solution. Some large aggregates (4–6 mm) of the Wahiawa soil broke into smaller aggregates dur-

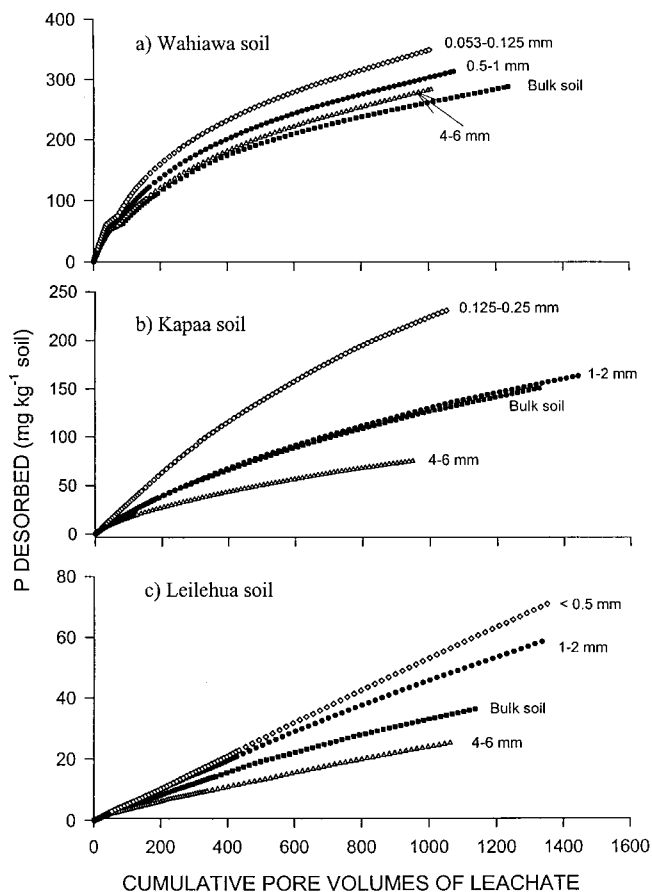


Fig. 2. Phosphorus desorption from aggregates size fractions of the Wahiawa, Kapaa, and Leilehua soils after P was applied to the bulk soils. Standard errors of the expanded Elovich equation estimated at mean value for aggregate sizes 0.053 to 0.125, 0.5 to 1, 4 to 6 mm, and bulk soil were 2.85, 2.64, 2.58, and 2.58 for the Wahiawa soil. The values for aggregate sizes 0.125 to 0.25, 1 to 2, 4 to 6 mm, and bulk soil were 0.78, 0.50, 0.59, and 0.59 for the Kapaa soil. The values for aggregate sizes <0.5, 1 to 2, 4 to 6 mm, and bulk soil were 0.19, 0.13, 0.18, and 0.09 for the Leilehua soil.

ing leaching. At the completion of leaching, the entire dried sample of the 4- to 6-mm aggregate fraction of the Wahiawa soil passed a 2-mm sieve and 19% of the sample passed a 1-mm sieve. For the other soils with strong aggregation, however, aggregate recoveries exceeded 92%.

### Phosphorus Desorption from Separated, Phosphorus-Enriched Aggregates

In the above section, the effects of aggregate size and extractable P level in the aggregate fraction on P desorption were not distinguishable. In the following comparison, the same amount of P was added to each previously separated aggregate fraction, equilibrated, and solution P levels measured. Thus, the difference in P release among aggregates should reflect only the effect of aggregate size, rather than redistribution and sorption among aggregate sizes as described in the above, where P was added before aggregates were separated. Phosphorus desorption from large aggregates (4–6 mm) in this case was greater than that from small aggregates (<0.5 mm) at the beginning of leaching treatment (Fig.

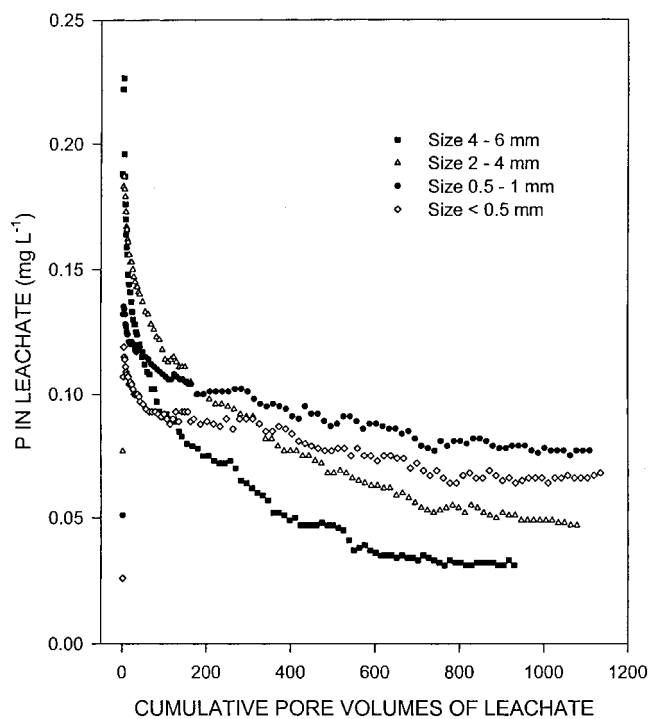


Fig. 3. Effect of aggregate size on P in leachate. A rate of 800 mg P kg<sup>-1</sup> was added to separated aggregates of the Leilehua soil.

3). The higher initial solution P in leachates indicates less P sorbed by the large aggregates during the incubation period. The decreased P retention with increased aggregate size is consistent with the finding that initial sorbed P was mainly on the outer surface of aggregates (Gunary et al., 1964; Willet et al., 1988; Linqvist et al., 1997).

The P concentration in leachate from the large aggregates initially was greater than that from small aggregates (Fig. 3). This may reflect a lack of accessibility of reactive sites within aggregates by P. The ratio of directly accessible reactive sites represented by the sample outer surface area in relation to the sample mass increases with decreased aggregate diameter assuming a spherical aggregate size (Table 3). Thus, more P release will be expected from small aggregates if P contents in differing aggregate fractions are the same.

### Comparison of Kinetic Models

Goodness of fit of the kinetic equations to the data was evaluated with the coefficient of determination ( $r^2$ )

Table 3. Ratio of the accessible outer spherical surface to soil mass for differing aggregate fractions.

Size	Diameter†	Ratio of outer surface to soil mass‡
	mm	m <sup>2</sup> kg <sup>-1</sup>
4-6	5.066	1.18
2-4	3.107	1.93
0.5-1	0.777	7.72
<0.5	0.315	19.05

† Diameter of each aggregate fraction was calculated on a volume-weighted basis using equation (Addiscott et al., 1983).  
‡ Outer surface was calculated by weighted mean diameter.

**Table 4. Coefficients of determination ( $r^2$ ) and standard errors (SE) for several kinetic equations describing P release from the three soils and differing aggregate fractions.**

Sample	Parabolic diffusion		Power function		Simple Elovich		Expanded Elovich	
	SE	$r^2$	SE	$r^2$	SE	$r^2$	SE	$r^2$
<b>Wahiawa soil</b>								
Bulk soil (<2 mm)	5.66	0.996	6.86	0.952	25.38	0.923	2.58	0.999
Size 4–6 mm	3.43	0.999	4.90	0.967	27.15	0.908	2.58	0.999
Size 0.5–1 mm	5.75	0.997	7.20	0.953	27.68	0.923	2.64	0.999
Size 0.053–0.125 mm	6.86	0.996	8.72	0.947	30.51	0.925	2.85	0.999
<b>Kapaa soil</b>								
Bulk soil (<2 mm)	4.19	0.993	1.97	0.969	19.21	0.850	0.59	1.000
Size 4–6 mm	1.62	0.996	0.68	0.978	9.03	0.862	0.59	0.999
Size 1–2 mm	4.62	0.993	2.27	0.968	20.95	0.849	0.50	1.000
Size 0.125–0.25 mm	9.03	0.987	4.04	0.963	32.35	0.828	0.78	1.000
<b>Leilehua soil</b>								
Bulk soil (<2 mm)	1.76	0.976	0.36	0.979	5.27	0.788	0.09	1.000
Size 4–6 mm	1.29	0.972	0.10	0.996	3.17	0.781	0.18	1.000
Size 1–2 mm	3.51	0.963	0.33	0.990	8.91	0.759	0.13	1.000
Size <0.5 mm	5.03	0.948	0.21	0.997	11.43	0.730	0.19	1.000
<b>P added to separated aggregates</b>								
Size 4–6 mm	0.91	0.998	1.07	0.960	6.15	0.883	0.14	1.000
Size 2–4 mm	1.92	0.993	1.05	0.968	8.86	0.858	0.15	1.000
Size 0.5–1 mm	4.49	0.974	0.44	0.989	12.37	0.800	0.13	1.000
Size <0.5 mm	3.99	0.974	0.58	0.985	11.12	0.800	0.14	1.000

and SE (Table 4). Conformity of P desorption data to the parabolic diffusion equation suggested that P release from the soil may be consistent with diffusion-controlled transport processes, probably with the rate-limiting step being the movement of P through a diffusion layer to the leaching solution. This diffusion layer is probably the unstirred water film surrounding outer aggregate surfaces or water films on surfaces within the aggregate itself. In view of the low SE of the power function, it seems to be an improvement over the parabolic equation, except for the Wahiawa soil and its aggregate fractions.

The simple Elovich equation provided the poorest fit among the four equations evaluated in describing P desorption. With the expanded form of the Elovich equation, the description of P desorption from the soil and aggregate fractions improved dramatically (Table 4). The superiority of the expanded Elovich equation over the simplified equation in describing P desorption has been documented elsewhere (Polyzopoulos et al., 1986; Raven and Hossner, 1994). In contrast to the simple Elovich equation, the expanded form of this equation mathematically allows for more flexibility in the curvature of the kinetic equation. This equation has been used previously to describe many kinetic processes

including bulk and surface diffusion (Sparks, 1986; Allen et al., 1995). In addition, its simplicity makes it attractive for descriptive purposes and for use in combination with more complex equations, where mechanistic P desorption equations are not available or too complex (Raven and Hossner, 1994).

### Effects of Aggregate Size on Phosphorus Supply in the Leilehua Soil

The total P content of soybean and lettuce shoots, root dry weights, and the root/shoot ratios were significantly influenced by aggregate size and P additions (Table 5). There were interactions between P addition and aggregate size for the total P content in soybean shoots, the roots of lettuce, and the root/shoot ratio for both soybean and lettuce.

### Total Phosphorus in Shoots

The total P content in soybean and lettuce shoots of plants grown in large aggregates (2–6 mm) was greater than that in plants grown in small aggregates (<0.5 mm) (Fig. 4). Shoot dry weight showed roughly the same trends as the P content (data not shown), so only P content is discussed here. These results were consistent

**Table 5. Analysis of variance table for the total P in shoots and root dry weights of soybean and lettuce.†**

Treatment	df	F value					
		Soybean			Lettuce		
		P content	Root	Root/shoot	P content	Root	Root/shoot
		mg P pot <sup>-1</sup>	g pot <sup>-1</sup>		mg P pot <sup>-1</sup>	g pot <sup>-1</sup>	
Aggregate size	3	17.69**	7.05**	11.92**	30.34**	71.21**	4.61
P rate	4	158.50**	14.83**	1.71NS‡	332.80**	416.60**	7.68**
Size × P rate	12	3.56**	1.77NS	4.03*	2.60NS	5.16**	3.05**
Block	2	1.65NS	1.52NS		1.25NS	1.73NS	

\* Significant at the 0.05 probability level.

\*\* Significant at the 0.01 probability level.

† A fixed model was used, and logarithmic transformation was used for the lettuce data.

‡ NS is not significant at the 0.05 probability level.

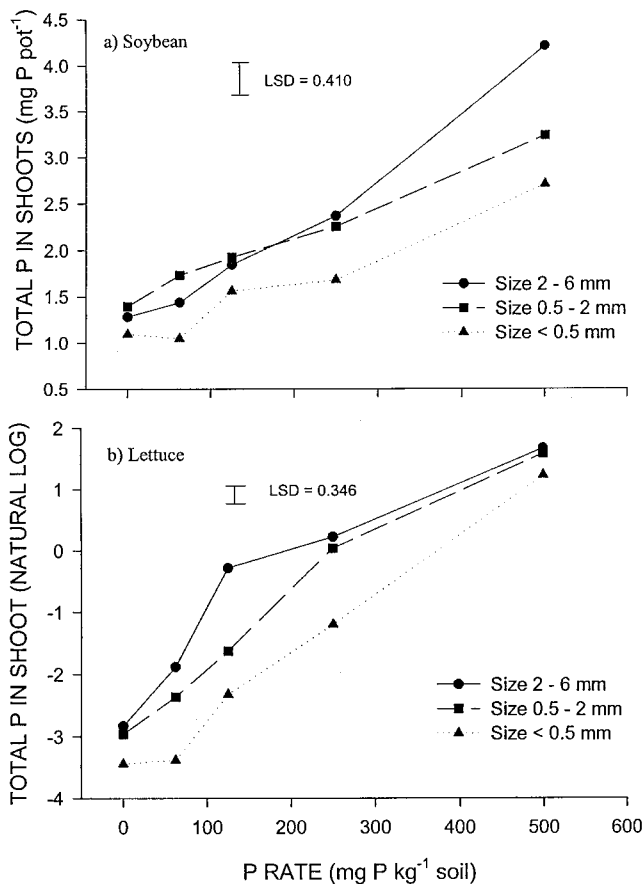


Fig. 4. Effect of aggregate size on the total P in soybean and lettuce shoots on the Leilehua soil. Error bars represent one LSD at  $P = 0.05$ . The total P in the lettuce shoots was natural logarithmically transformed.

with the greater decrease in  $0.5 M \text{NaHCO}_3$ -extractable P recovered from large aggregates at harvest than from small aggregates. The difference in the soil extractable P before planting and after harvesting was calculated and the relationships between the total P in shoots and the difference in the extractable P are shown in Fig. 5. Phosphorus uptake was correlated with the decrease in extractable P. The change in the extractable P, however, was a better predictor of P in soybean shoots than in lettuce shoots. Continuous sorption of the added P by soil during the plant growth period in addition to plant uptake probably also contributed to the decrease in extractable P. In addition, the effects of aggregate size on the P content in soybean shoots were dependent on P additions because there were significant interactions between aggregate size and P rate (Table 5). The difference in P content in soybean shoots between the 2- to 6-mm aggregate fraction and the  $< 0.5$  mm aggregate fraction became greater with increased P rates (Fig. 4a).

The greater total P in plant shoots grown in the large aggregate fraction corresponded with the greater initial rate of P release from this fraction in the column leaching study. Phosphorus retention was reduced in large aggregates (Linguist et al., 1997; Wang, 1997) and, consequently, more P remained in solution. Thus, more recently added P was available to plants from large aggregates.

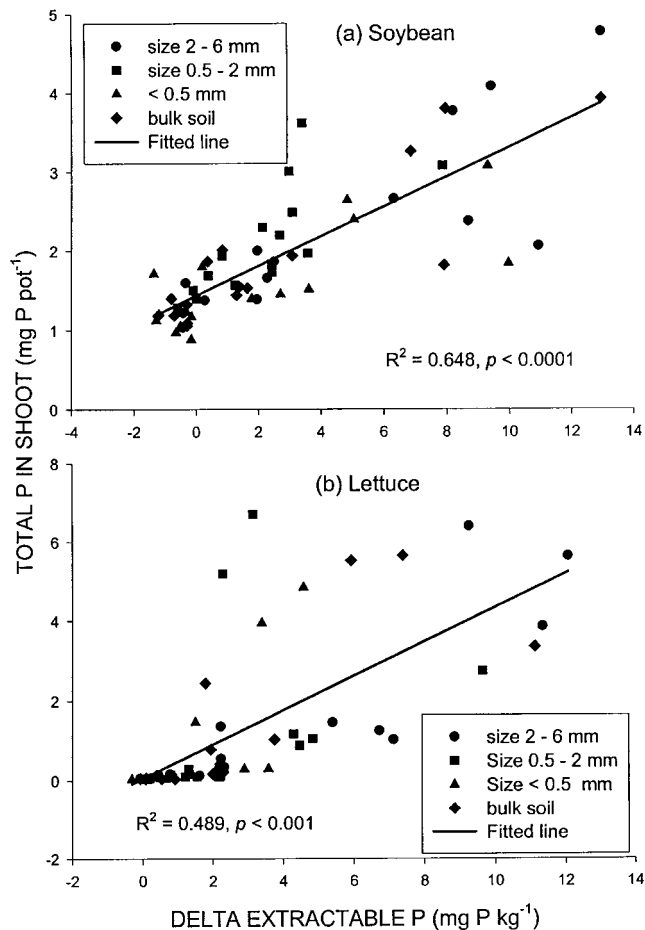


Fig. 5. Relationship between total P in shoots and the difference in  $0.5 M \text{NaHCO}_3$ -extractable P before planting and after harvesting (Delta P).

With increased leaching, however, a greater decrease in P desorption rate was observed from large aggregates than from small aggregates (Fig. 3). This suggested that P uptake by plants would be reduced from large aggregates after most of easily desorbed P is removed. With depletion of P around the aggregates, P diffusion from the inside of the aggregates to the outside, and the accessibility of roots to P within the aggregates, could become important influences on P supply.

#### Root Growth and Ratio of Root to Shoot

Dry weights of roots grown in the small aggregate fraction ( $< 0.5$  mm) were less than those of plants grown in the large aggregate fraction (2–6 mm) for both soybean and lettuce for all but the zero P treatment for soybean (Fig. 6). The ratios of root to shoot for both soybean and lettuce decreased with aggregate size and P rate (Fig. 7). The decreased ratio with increased P rate is consistent with the finding that the ratio decreases with increased P availability (Cassman et al., 1980).

The greater root growth of plants growing in large aggregates may be attributed to several factors. In this greenhouse experiment, P was added to separated aggregate fractions, and available P in the larger aggregates was greater than in the smaller aggregates. This

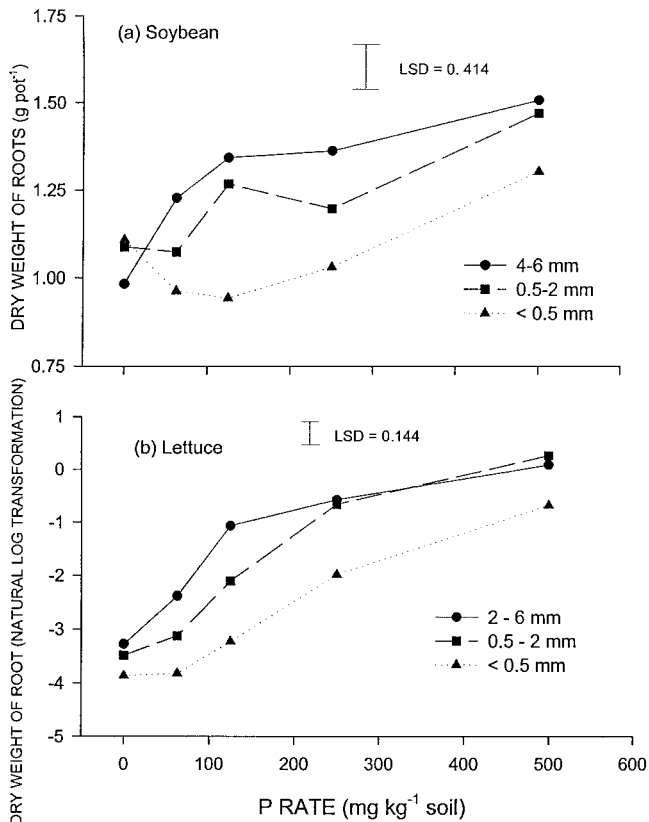


Fig. 6. Effect of aggregate size on the root dry weights of soybean and lettuce on the Leilehua soil. Error bars represent one LSD at  $P = 0.05$ . The root dry weight of lettuce was logarithmically (natural) transformed.

suggests that greater P availability in treatments with larger aggregate fraction increased root growth. This hypothesis was further supported by the root/shoot ratios for both soybean and lettuce, which decreased with increased aggregate sizes. Cassman et al. (1980) also observed a decrease in the root/shoot ratio for soybean with increasing P supply. Therefore, the higher root/shoot ratios for both soybean and lettuce in the smallest aggregate fraction treatment (<0.5 mm) strongly suggest that soybean and lettuce were more P-deficient in these treatments than in those with larger aggregate fractions.

## CONCLUSIONS

Our results suggest that soil P extraction procedures that destroy soil aggregates during extraction may overestimate P fertilizer requirements by exposing P sorption sites that would otherwise be excluded from the leaching solution. For example, the P requirement to attain a solution P of 0.03 mg P L<sup>-1</sup> using the Fox and Kamprath method (Fox and Kamprath, 1970) was 100 mg P kg<sup>-1</sup> greater than the P requirement estimated while preserving natural aggregates of the Haiku soil (Linguist et al., 1997). This is reflected by field results such as those by Cassman et al. (1993), who found that the application of 100 kg P ha<sup>-1</sup> to the Haiku soil produced the maximum yield of soybean, although the recommended P application rate for soybean, based on the

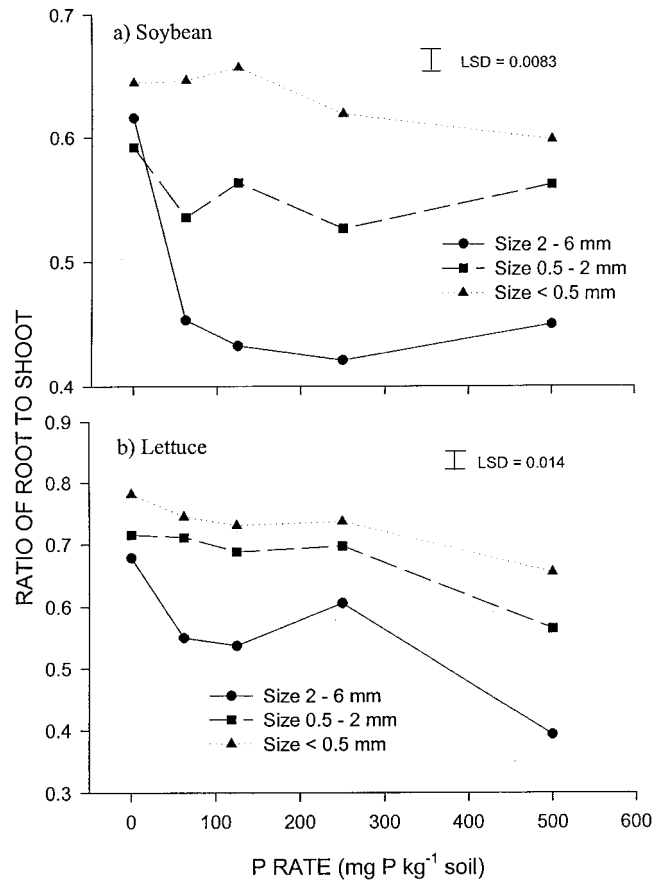


Fig. 7. Effect of aggregate size on the ratio of root to shoot for both soybean and lettuce on the Leilehua soil. Error bars represent one LSD at  $P = 0.05$ .

Fox and Kamprath method, was more than 500 kg P ha<sup>-1</sup> (Cassman et al., 1981).

Some highly weathered soils such as the Wahiawa with a smaller geometric mean diameter (GMD) did not exhibit the strong effects of aggregation on P sorption. Tentatively, GMD may be a way to quantify this effect, although one sample of three soils was too few to confirm GMD as a measure.

The reduced P retention and increased P release with increased aggregate size suggests that P buffer coefficients would be better estimated by including aggregate size. For soils with a wide range of mineralogical composition but relatively high clay contents, P buffer coefficients were more accurately predicted by including the soil P sorption site density and reactive mass (a fraction of the total soil mass in the surface aggregates where newly added P can be sorbed) (Wang et al., 2000). Thus, considerations of the aggregate effects may improve the relationship between extractable P, P supply, and crop yield and eventually improve the precision of P diagnosis and recommendation on well-aggregated soils.

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## REFERENCES

- Addiscott, T.M., V.H. Thomas, and M.A. Janjua. 1983. Measurement and simulation of anion diffusion in natural soil aggregates and clods. *J. Soil Sci.* 34:709-721.
- Allen, E.R., D.W. Ming, L.R. Hossner, and D.L. Henninger. 1995. Modeling transport kinetics in clinoptilolite-phosphate rock system. *Soil Sci. Soc. Am. J.* 59:248-255.
- Amer, F., C.A. Bouldin, C.A. Black, and F.R. Duke. 1955. Characterization of soil phosphorus by anion exchange resin adsorption and  $P^{32}$ -equilibration. *Plant Soil* 6:391-408.
- Barrow, N.J. 1983. On the reversibility of phosphate sorption by soils. *J. Soil Sci.* 34:751-758.
- Cassman, K.G., P.W. Singleton, and B.A. Linquist. 1993. Input/output analysis of the cumulative soybean response to phosphorus on an Ultisol. *Field Crops Res.* 34:23-26.
- Cassman, K.G., A.S. Whitney, and R.L. Fox. 1981. Phosphorus requirements of soybean and cowpea as affected by mode of N nutrition. *Agron. J.* 73:17-22.
- Cassman, K.G., A.S. Whitney, and K.R. Stockinger. 1980. Root growth and dry matter distribution of soybean as affected by phosphorus stress, nodulation, and nitrogen source. *Agron. J.* 73:17-22.
- Chen, G., R.S. Yost, Z.C. Li, X. Wang, and F.R. Cox. 1997. Uncertainty analysis for knowledge-based decision aids: Application to PDSS (Phosphorus Decision Support System). *Agric. Syst.* 55:461-471.
- Chien, S.H., and W.R. Clayton. 1980. Application of Elovich equation to the kinetics of phosphate release and sorption in soils. *Soil Sci. Soc. Am. J.* 44:265-268.
- Cornforth, I.S. 1968. The effect of size of soil aggregates on nutrient supply. *J. Agric. Sci. (Cambridge)* 70:83-85.
- Gunary, D., E.G. Hallsworth, and D.V. Crawford. 1964. The experimental study of the mobility of ions in soil, with particular reference to phosphorus. p. 149-156. *Experimental pedology. Proc. Univ. Nottingham 11th Easter Sch. Agric. Sci.*
- Fox, R.L., and E.J. Kamprath. 1970. Phosphate sorption isotherms for evaluating the P requirements of soils. *Soil Sci. Soc. Am. Proc.* 34:902-907.
- Kafkafi, U., A.M. Posner, and J.P. Quirk. 1967. Desorption of phosphate from kaolinite. *Soil Sci. Soc. Am. Proc.* 31:348-352.
- Kuo, S., and E.G. Lotse. 1974. Kinetics of phosphate adsorption and desorption by hematite and gibbsite. *Soil Sci.* 116:400-406.
- Jury, W.A., W.R. Gardner, and W.H. Gardner. 1991. *Soil physics*. 5th ed. John Wiley and Sons, New York.
- Linquist, B.A., P.W. Singleton, R.S. Yost, and K.G. Cassman. 1997. Aggregate size effects on the sorption and release of phosphorus in an Ultisol. *Soil Sci. Soc. Am. J.* 61:160-166.
- Misra, R.K., A.M. Alston, and A.R. Dexter. 1988. Root growth and phosphorus uptake in relation to the size and strength of soil aggregates. I. Experimental studies. *Soil Tillage Res.* 11:103-116.
- Murphy, J., and J.P. Riley. 1962. A modified single solution method for the determination of phosphate in natural waters. *Anal. Chim. Acta.* 27:31-36.
- Olsen, S.R., C.V. Cole, F.S. Watanabe, and L.A. Dean. 1954. Estimation of available phosphorus in soils by extraction with sodium bicarbonate. USDA Circ. 939. U.S. Gov. Print. Office, Washington, DC.
- Polyzopoulos, N.A., V.Z. Keramidas, and A. Pavlatou. 1986. On the limitations of the simplified Elovich equation in describing the kinetics of phosphate sorption and release from soils. *J. Soil Sci.* 37:81-87.
- Raven, K.P., and L.R. Hossner. 1994. Soil phosphorus desorption kinetics and its relationship with plant growth. *Soil Sci. Soc. Am. J.* 58:416-423.
- Rajbhandari, N.P. 1991. Analysis of competition and phosphorus response in maize/soybean and maize/rice intercrops in relation to soil phosphorus availability in different environments. Ph.D. dissertation. Dep. of Agronomy and Soil Sci., Univ. of Hawaii, Honolulu.
- Sawhney, B.L. 1977. Predicting phosphate movement through soil columns. *J. Environ. Qual.* 6:86-89.
- Sparks, D.L. 1986. Kinetics of reactions in pure and mixed systems. p. 83-145. *In* D.L. Sparks (ed) *Soil physical chemistry*. CRC Press, Boca Raton, FL.
- Statistical Science. 1995. S-PLUS guide to statistical and mathematical analysis. Version 3.3. StatSci, MathSoft, Seattle, WA.
- van der Zee, S.E.A.T.M., and A. Gjaltema. 1992. Simulation of phosphorus transport in soil columns. I. Model development. *Geoderma* 52:87-109.
- Vig, A.C., and G. Dev. 1979. Kinetics of phosphate desorption in soils. *J. Nucl. Agric. Biol.* 8:62-66.
- Wang, X. 1997. Phosphorus sorption, desorption, and availability in Oxisols and Ultisols as influenced by soil aggregate size. Ph.D. diss. Univ. of Hawaii, Honolulu.
- Wang, X., J. Jackman, R.S. Yost, and B.A. Linquist. 2000. Predicting soil phosphorus buffer coefficients using potential sorption site density and soil aggregation. *Soil Sci. Soc. Am. J.* 64:240-246.
- Watanabe, F.S., and S.R. Olsen. 1965. Test of an ascorbic acid method for determining phosphorus in water and  $NaHCO_3$  extracts from soil. *Soil Sci. Soc. Am. Proc.* 29:677-678.
- Wiersum, L.K. 1962. Uptake of nitrogen and phosphorus in relation to soil structure and nutrient mobility. *Plant Soil* 16:62-70.
- Willett, I.R., C.J. Chartres, and T.T. Nguyen. 1988. Migration of phosphate into aggregated particles of ferrihydrite. *J. Soil Sci.* 39:275-282.
- Yang, J.E., and E.O. Skogley. 1992. Diffusion kinetics of multinutrient accumulation by mixed-bed ion-exchange resin. *Soil Sci. Soc. Am. J.* 56:408-411.