PHOSPHORUS SORPTION, DESORPTION AND AVAILABILITY IN OXISOLS AND ULTISOLS AS INFLUENCED BY SOIL AGGREGATE SIZE

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ABSTRACT

Phosphorus (P) limits food and fiber production in most regions of the tropics. The diagnosis and prediction of nutrient P requirements continues with low precision and high uncertainty. Some recent estimates suggest that predictions may be in error by as much as 50%. Initial data suggest that the high degree of soil aggregation common in highly weathered soils may affect P sorption. This study was conducted to determine the effects of soil aggregate size on P availability in order to improve P requirement prediction. The soils studied were highly weathered Typic Kandihumult (Leilehua), Anionic Acrudox (Kapaa), and Rhodic Eutrustox (Wahiawa), that represent high P sorption and a range in soil aggregation. Samples were collected from field plots of P experiments, where P had been applied 3-7.5 years before. For each soil, eight aggregate size fractions of < 0.053, 0.053-0.125, 0.125-0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, and 4-6 mm were obtained using a dry-sieving method. For the Kapaa and Leilehua soils, sodium bicarbonate extractable P in aggregates increased up to 5-fold with decreasing aggregate size when P had been applied to soils. The extractable P did not increase with decreasing aggregate size on all soils where no P had been applied and even where P had been added to the Wahiawa soil. An incubation study showed that the increased extractable P was due to more sorbed P in small aggregates after P was added to a mixture of aggregates of different size. In contrast, P sorption decreased, and extractable P increased with increasing aggregate size after P was added to the separated aggregate fractions. The total P in soybean and lettuce shoots grown in larger aggregates (2-6 mm) was greater than in smaller aggregates (<0.5 mm) after P was added to the separated aggregate fractions. The reduced P sorption and increased P desorption with increasing aggregate size suggests that an improved prediction of the P buffer coefficients and P requirements in crop production systems could be achieved considering soil aggregate size distribution.

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CHAPTER 1 INTRODUCTION

Phosphorus (P) in soils undergoes sorption and desorption reactions with soil components, and its availability to plants may be limited by these reactions. The extent of the sorption-desorption is affected by the type of mineral, the surface area, temperature, pH, soil physical properties such as microstructure, or aggregation, etc. Fertilizers can be applied to increase P in solution. Consequently, knowledge of the nature and reactions of fertilizer P with soils will improve P fertilizer management. Considerable effort has been made to render native phosphorus more available and to improve the efficiency of use of phosphate compounds as fertilizer. But on the whole such experiments have not been very successful. Such efforts have been made difficult by our lack of knowledge of P dynamics in soils. We have recognized the need for this knowledge, but despite intensive work on the subject for many years the mechanisms of phosphorus retention by soils are still inadequately understood.

P fixation or retention is generally considered as the transformation of soluble forms of P into less soluble ones after they react with the soil (Sanchez and Uehara, 1980). Applying P fertilizer to acid soils often results in low fertilizer efficiency because acid soils sorb large amounts of P through either P adsorption or precipitation with Fe and Al compounds and crystalline and x-ray amorphous colloids of low silica-sesquioxides ratios present in acid soils, or both. The relative importance of these mechanisms varies with soil properties and experimental conditions imposed during P investigation. It should be noted that the phosphate retained by soils is not necessarily fixed. If the phosphate retained by soils could be released to soil solution later at a reasonable rate for plant uptake, then P retention is advantageous rather than disadvantageous to fertility management. Long-term fertilizer experiments at Rothamsted Experimental Station, which have been running for over 100 years, indicate the apparent utility of long-term P retention in soil (Ross, 1989). There, however, is also much evidence to suggest that its effectiveness in terms of crop uptake decreases through time. This leads to examination of mechanisms controlling the slow, long-term reactions of phosphate with soils because of their effects on the availability and maintenance of phosphate according to soil management. The actual mechanisms are somewhat unclear although the existence of a slow reaction between phosphate and soil components is well documented.

Recent studies of P diffusion within Fe and Al oxides have been emphasized because of its presumed role in P slow reactions in soils (Parfitt et al., 1989; Torrent et al., 1990; Torrent et al., 1992). It has been reported that the diffusion of P within mineral aggregates probably depends on the degree of crystallinity or porosity of Al and Fe oxides (Barrow et al., 1988; Parfitt, 1989; Torrent et al., 1990; Torrent et al., 1992). The P slow reaction with the soil sample may be more pronounced than with the pure minerals due to soil aggregation. Soil aggregation may affect P penetration into the sorbing surface sites in the aggregates. Accordingly, the slow reaction of phosphate by aggregated soils might be attributed to the migration of P to surface sorption sites of decreasing accessibility within aggregates, and/or diffusion of P through surface micropores in intra-aggregates. Its importance lies in rendering phosphate unavailable to crops.

Phosphate within the soil aggregates may be extracted by soil-tests due to aggregate destruction during the preparation of soil samples and extraction procedures. The extractable P from sorption sites deep within the aggregates may actually have less bioavailability to plants than P near the exterior surface of soil aggregates. One of the possible reasons is that plant root systems have low access to the phosphate within the soil aggregates. The phosphate may not be able to move out of the aggregates because of limited P diffusion through micropores of intra-aggregates. Cox (1992) found a range in soil P critical levels with time in the field. Field trials in a Hawaiian soil indicated that the critical levels of soil phosphate increased with time (Linquist, 1995).

Effects of aggregate size on root growth and phosphorus uptake by plants have been examined (Wiersum, 1962; Cornforth, 1968; Misra et al., 1988 a). A general conclusion has been reached that phosphorus uptake from small aggregates is higher than from large aggregates. This conclusion is based on the fact that root growth decreases with increasing aggregate size and, hence, strength of aggregates. However, the level of extractable-P of aggregated soils change aggregate size. Linquist showed (1995) that extractable-P (the sum of the $NaHCO_3$, and NaOH, and the residual P fraction from the procedure of Hedley et al., 1982) increased in the P applied sample as the mean aggregate diameter decreased from 3.4 to 0.75 mm, however for aggregates below 0.75 mm the P content of both the soil sample with added P and the control without added P decreased with decreasing mean aggregate diameter. These results suggest that P supply may be influenced by the distribution of applied P among the aggregates and possibly by differential P uptake by plants from the different aggregates.

These conclusions point out the importance of effects of soil physical properties on P sorption and desorption, P slow reaction, and the availability to crops; these concepts haven't been considered in controlling phosphate dynamics. The purpose of this dissertation is to develop a methodology to evaluate the effects of soil aggregation and microstructure on the processes of P sorption and desorption (release) and its availability in order to predict P availability, buffer coefficients and long term residual P. The objectives were to: 1) elucidate the effect of soil microstructure and aggregation on P sorption and desorption; 2) determine the P distribution among aggregates of varying size; 3) predict P migration into soil aggregates in order to identify the effect of soil aggregation and its microstructure on reaction rate; 4) determine the effects of the aggregate size on root growth and P uptake in a greenhouse experiment; and 5) attempt to predict P buffer coefficients and residual P from improved knowledge of the effects of soil aggregation.

AGGREGATION AND MICROSTRUCTURE

All soils that contain colloidal materials exhibit aggregation where clusters of particles of different sizes remain associated when the soil is stressed mechanically by tillage, drying and wetting. The nature and size distribution of aggregates and its converse, pore space, is referred to as soil structure and plays an important role in soil physical properties (Wild, 1988) and hence soil fertility. Although it is often speculated why crops respond favorably to good soil structure, experiments are rare (Horn et al., 1994). Emmerson et al. (1978) showed there were interactions between soil structure, water status of structured soils, soil aeration and root growth. Dexter (1988) defined soil structure as the spatial heterogeneity of the different components or properties of soil at various scales. Bouma (1990) among others has repeatedly emphasized that not only the determination of the amount and diameter of pores but also the function and the distribution of the solid phase and pores as well as their connection, define ecologically important soil properties. This is especially true with respect to the accessibility of the aggregate surface to water, ions and gases (Horn et al., 1994).

The geometry of the soil pores, to a large extent, controls the retention, availability and rate of water movement, and thus solute movement. To a lesser extent pore geometry affects the aeration, and soil permeability to roots. Note that soil pores are not simple tubes, but irregular non-rigid space interconnecting through necks. It is the complex geometry of interconnections that largely controls water and solute release and rates of movement.

If soil structure is of interest because of its effects on soil fertility, then it is most usefully analyzed in terms of its pore characteristics. For example, a soil with a high proportion of pore volume in pores finer than 1 μm necessarily has a large pore surface, which to a large extent, affects the retention of most nutrients in soil. Fine clays in the clay fraction have most pores of less than 0.1 μm in diameter (Wild, 1988). This is one of the reasons why clay content is a major factor in controlling P sorption capacity. However, since pores are themselves controlled by the distribution and stability of the soil solid, then it is the aggregation of the solids that is important to understand the factors involved in structure development and preservation.

ION TRANSPORT IN AGGREGATED SOILS

Solute transport in structured soils is classified as being in "mobile" and "immobile" phases because most soils are heterogeneous porous media consisting of micropores in intra-aggregates and macropores in inter-aggregates. The mobile phase is limited to the centers and the inner peripheries of inter-aggregate pores. Liquid in the "immobile" phase, however, percolates very slowly through the micropores within the aggregates. Exchange processes between the two phases are limited because fast flow through the inter-aggregate pores removes the mobile phase before equilibrium can be established. Consequently, transport in such systems is often characterized by physical or transport nonequilibrium phenomena. These phenomena have usually been ascribed to the presence of immobile phases within the porous medium, which results in physical nonequilibrium (Brusseau and Rao, 1990).

Transport through the inter-aggregate pores can be described with convection-dispersion equations (Selim et al., 1985), whereas exchange of ions between the mobile (inter-aggregate pores) to the immobile phase (intra-aggregate pores) can be described with diffusion-controlled equations. This exchange between inter-aggregate pores and intra-aggregate pores may be due to high flow velocity in the inter-aggregate pores.

Several mechanisms are involved in the solute-transport process for a system representative of the mobile-immobile concept: (1) advective-dispersive transport from bulk solution to the boundary layer (i.e. adsorbed water surrounding the sorbent), (2) diffusive transport across the adsorbed water (i.e. film diffusion); and (3) pore and/or surface diffusion within the immobile region (i.e. intra-aggregate diffusion) (Brusseau and Rao, 1990). Any or all of these three components may be a rate-limiting step. To simplify, it is usually assumed that one of the three steps is slow relative to the other two and that it may, therefore, be designated as the primary rate-limiting step.

The advective-flow domain is generally assumed to be well mixed, thus minimizing the importance of mass-transfer resistance within these regions. Intra-aggregate diffusion appears to control solute uptake for the majority of the reaction period while it appears that film diffusion controls the solute uptake rate initially (Brusseau and Rao, 1990). Intra-aggregate diffusion, therefore, is usually the transfer process designated as the rate-limiting step. Note that sorption at the sorbent-liquid interface is assumed to be instantaneous; the rate at which the solute is transported to and from this interface, therefore, controls the attainment of equilibrium (Brusseau and Rao, 1990).

The inter- and intra-aggregate pore system affects both the accessibility of exchange sites and adsorption and desorption because the accessibility of solid surface to solutions is reduced by aggregation (Horn et al., 1994). Convective ion transport is much smaller in single aggregates compared with bulk soil and, especially, with the homogenized material for a constant amount of water (Horn and Tauber, 1989). Ion diffusion out of single aggregates is reduced compared with the bulk soil at a given time. Several reasons for this difference have been proposed and summarized by Horn et al. (1994) as follows: (1) the ratio of directly accessible reaction sites represented by the sample outer surface to the sample mass decreases with increasing aggregate diameter, assuming a spherical aggregate shape; (2) flow length increases with aggregate size; (3) the average pore size and the pore continuity in single aggregates is much smaller owing to a higher clay content at the outer skin; and (4) the bulk density of single aggregates is greater than that of the bulk soil.

The effect of the accessibility of the particle surface within aggregates on nutrient release by diffusion has been investigated for K by Horn and Taubner (1989). In their experiments to determine cumulative potassium release rates out of single aggregates, of structured bulk soil, and of homogenized soil material (< 2 mm) under saturated conditions, the release rates per mass unit of soil were the highest for the homogenized material. In aggregates, release of K from internal reaction sites was retarded. The larger the aggregates, the smaller the release rates were at a given bathing solution. Bhadoria et al. (1991 a, b) further quantified the impedance factor *f* for chloride diffusion in soil as affected by bulk density and water content. An increase in bulk density from 1.38 to 1.76 Mg m^{-3} at a constant gravimetric moisture content of 7% decreased *f* by a factor of 3, while at a water content greater than 10%, *f* increased linearly with increasing bulk density.

SOIL STRUCTURE EFFECTS ON P SORPTION AND RELEASE

Soils contain three sizes of pores through which ions move to plant roots (Vaidyanathan and Talibudeen, 1968): (1) inter-aggregate pores, which carry the main body of ions at water content above field capacity; (2) large intra-aggregate pores, which become important in ion-transport when the thickness of water films in inter-aggregate approaches the diameter of intra-aggregate spaces; and (3) smaller intra-aggregate pores, which permit ion transport to roots only via the other two kinds of pores. Measurements of the rates at which soil P is released into the soil solution and of isotopic exchange between soil P and that in solution suggest that most soil P is associated with intra-aggregate pores in which the distribution between larger and smaller pores depends on the reaction time of P with soil (Talibudeen, 1958). Smaller amounts of phosphate associated with the surfaces of inter-aggregate pores (and possibly some of the larger continuous intra-aggregate pores) move at least 100 times faster and are mainly responsible for P supply to roots via water in the inter-aggregate space (Vaidyanathan and Talibudeen, 1968). The slower moving but usually larger, store of phosphate in intra-aggregate pores helps to maintain the concentration of phosphate in inter-aggregate pores.

That phosphate diffuses to sorption sites in micropores of Fe and Al hydrous oxides (on crystal surfaces, between domains of contiguous crystals) and in micropores of soil aggregates is a hypothesis compatible with observed positive effects of time and concentration in promoting more P sorption. Micro- and meso-porosity was found to enhance the slow P reaction by lepidocrocite (Cabrera et al., 1981; Madrid and de Arambarri, 1985) and is likely to have the same effect on natural goethites (Parfitt, 1989). Willett et al. (1988) studied P sorption in ferrihydrite and attributed the P slow reaction to the migration of phosphate to surface sorption sites of decreasing accessibility within the ferrihydrite particles. Synthetic goethites should also produce the "slow reaction" due to their large specific area and porous aggregates (Torrent et al., 1990). Later, these authors (Torrent et al., 1992) confirmed that the extent of P slow reaction is correlated to the ratio of micropore surface area to total surface area in goethite-rich natural materials, as well as to oxalate-extractable Fe, which is an estimate of ferrihydrite content. Ferrihydrite impurities might affect the slow reaction by contributing to microporosity.

Studies of isotopic exchange ability of sorbed P have frequently found a pattern of fast rate of exchange followed by slow rate of exchange. This observed isotopic exchange of soil phosphate probably represents the combined effects of the accessibility of anion-exchanging sites in intra-aggregate pores to the bulk solution and the strength of binding of ions in these sites. Phosphate ions exchanging initially are probably those loosely held in the outer and larger pores; when these ions have exchanged, P diffusion through the inner and smaller intra-aggregate micropores controls the rate of transfer from soil to solution. The intra-aggregate diffusion coefficient probably, therefore, defines the internal structure and P-binding properties of soil aggregates, and, consequently, may be independent of added P (Vaidyanathan and Talibudeen, 1968).

Phosphorus desorption and isotopic data have been related to porosity of iron oxides, lepidocrocite and goethite (Cabrera et al., 1981) and soil microstructure (Vaidyanathan and Talibudeen, 1968; Staunton and Nye, 1989). Cabrera et al. (1981) attributed the presence of a component of the exchangeable P released very slowly to P sorbed on the surface of intra-aggregate pores. Staunton and Nye (1989) found that a much higher proportion of isotopic exchange is instantaneous in the exchange systems (suspension, solution circulating through soil, and moist incubated soil) than in the diffusion runs (isotope diffusion through moist soil). Clearly, the equilibrium and kinetic parameters obtained from isotopic exchange in a well-mixed soil cannot be used to predict the rate of change of concentration of phosphate isotope diffusing in soil. The kinetics of exchange in a diffusion system and in well-mixed soil are not limited by the same factors. They postulated that exchange of a diffusing isotope is limited by access to exchange sites, and not by reaction at the liquid-solid interface.

An attempt to explain differences in rates of adsorption and desorption of isotope have been made by applying diffusion theories to exchange data (Vaidyanathan and Talibudeen, 1968). They found that an 'intracrumb' diffusion mechanism controlled isotopic exchange of soil phosphate at exchange times greater than 20 h in the soils they used, depending on soil pH. But isotopic exchange of soil phosphate in the short time period was a composite effect of the film and intra-aggregate diffusion processes. In their studies, two models were proposed to enable mechanisms of both film and intra-aggregate diffusion to be used to account for the rate of isotopic exchange of soil phosphate.

The smallness (10^{-14} cm^2 per sec.) of the diffusion coefficient of the exchanging phosphate within the intrapores (Vaidyanathan and Talibudeen, 1968) suggests that this exchange process may play little part in supplying phosphate ions to plant roots, in which the initial semi-logarithmic rate process in phosphate exchange must play a significant role. Other work (Olsen and Watanabe, 1963; Bhadoria et al., 1991) showed that measurements of phosphate transport through packed soil crumbs gave diffusion coefficients between 10^{-7} to 10^{-9} cm^2 per second. Such values adequately account for P uptake by plants (Olsen and Watanabe, 1963) when the relationship between labile P of solid phase and P concentration in solution, the tortuosity of the intercrumb pathway and soil moisture content are considered. Phosphate flux, estimated from the diffusion coefficient of the intra-aggregates (Vaidyanathan and Talibudeen, 1968), is unlikely to contribute directly to phosphate uptake (at least by annual crops) from soils which have rapidly labile pools adequate for plant growth.

However, seasonal measurements of soil P intensity in dilute calcium chloride over several years show that it changes in a regular cycle, with a substantial decrease during maximum crop growth, followed by increase during the fall and winter "rest" periods (Blakemore, 1966; Garbouchev, 1966; Weaver et al., 1988). The P intensity and labile pool of phosphate of the soil can be decreased to different levels by extracting soil P with anion-exchange resins and mixed cation/anion-exchange resins. When the depleted soils are again incubated at field capacity their intensity and pool values for phosphate increase and may be fully restored (Vaidyanathan and Talibudeen, 1965). These new equilibrium values are attained after more than three months incubation. Vaidyanathan and Talibudeen (1968) believed that these "rest" or "incubation" periods during which "recovery" processes act, must relate to the intra-aggregate diffusion coefficient. Recent work (Magid and Nielsen, 1992) shows that the changes in inorganic P fractions follow the changes in soil moisture content inversely. All soil inorganic P fractions were at minimum in the cool moist winter period. They suggest that the variation in inorganic P may be explained by the physico-chemical processes (e.g. P desorption) influenced by the soil moisture content, and by effects of drying on the soil microbial biomass.

P UPTAKE IN RELATION TO AGGREGATE SIZE AND STRENGTH

Nutrient uptake by plants from soil depends on the ability of the plant root to absorb the nutrient, on the ability of soil to supply the nutrient, and on the accessibility of the nutrient as determined by the size and configuration of the root system. The structure and strength of the soil influence the configuration of the root system and hence nutrient uptake (Misra et al., 1988a). Studies of nutrient uptake with aggregates of varying sizes (Wiersum, 1962; Cornforth, 1968; Misra et al., 1988a) found that P uptake from small aggregates was higher than that from large aggregates. They explained their results by considering the low mobility of phosphate in soils and the inaccessibility of roots including root hairs to phosphate within large aggregates. For the phosphate mobility in soils, data published up to now indicate that roots can deplete phosphate only from a distance that coincides approximately with the length of the root hairs (Lewis and Quirk, 1967; Bhat and Nye, 1973; Misra et al., 1988a). In aggregated soil, plant roots may grow into voids within aggregates, or on the surface of aggregates. With increased aggregate size and aggregate strength, more roots tend to grow in voids and on the surface of aggregates, and their contribution to P uptake is less than that of roots growing through aggregates (Misra et al., 1988a). This is based on the assumption that roots growing within aggregates are able to extract more P than root growing outside aggregates. This assumption seems untested so far. Nevertheless, Misra et al. (1988b) demonstrated that root hairs had a strong influence on the accessibility of phosphorus to roots in a soil with considerable macrostructure. They found that, because root-hair length was greater with larger aggregates, the increased relative P uptake due to increased root-hair length compensates for the decreased relative P uptake due to increased aggregate size and strength.

Some other workers attempted to relate the effects of aggregate size on root growth and nutrient uptake to an increase in mechanical resistance adjacent to the soil-root interface with an increase in aggregate size. Voorhees et al. (1971) and Bradford (1980) reported that the strength of discrete aggregates affected the penetration and elongation of roots, and this may affect nutrient uptake. The availability of plant nutrients as a function of soil strength has gained attention recently. In studies with homogeneous soil, increased mechanical impedance caused by compaction was shown to prevent root development and increased root diameter, and nutrient availability was decreased (Boone and Veen, 1982; Castillo et al., 1982; Shierlaw and Alston, 1984). In agreement with those results, more recently Misra et al. (1988) reported that increased aggregate strength associated with increased aggregate size reduced root growth and P uptake by both cotton and sunflower in a soil.

Current studies have concentrated on the influence of soil structure on root development and ion movement, and therefore ion uptake. However, there is a lack of quantitative investigation and insight on the influence of aggregate size and soil aggregation on nutrient status in soils. Nutrient availability should be the main factor determining the nutrient uptake by plants given the other growth conditions are optimal. Studies of the effects of aggregate size on phosphate supply should consider the influences of aggregate size and aggregation on P sorption, desorption, and its availability to plants. Alberts and Moldenhauer (1981), who conducted a study on N and P transported by eroded soil aggregates of a Mollisol, observed that total N and extractable P (Bray I test) of uneroded soil aggregates separated by wet sieving progressively decreased for the 2- to 1-, 1- to 0.5-, and 0.5- to 0.21-mm aggregates. Nutrient (N and P) concentrations of the <0.05-mm particles were lower than those for the 2- to 0.5-mm aggregates, probably because smaller aggregates contained a smaller proportion of clay (a higher proportion of silt was found in their study). It was suggested that the extractable P concentration in the aggregates correlated positively with their finer particle contents (Alberts and Moldenhauer, 1981; Mbagwu and Piccolo, 1990).

In an experiment comparing reactions of inorganic P in solution and liquid manure P with soil aggregates, Bhatnagar and Miller (1985) found that the addition of inorganic P solution or the supernatant liquid from a centrifuged manure slurry increased the $NaHCO_3$-extractable P of large aggregates only slightly (around 20%). A greater increase in extractable P in large aggregates was observed when the smaller aggregates were arranged on top of the larger aggregates prior to addition of the liquid manure. In agreement with this result, Elliott (1986) found that when slaked (left air dry), native and cultivated soil, present in the microaggregate size classes, contained less organic C, N and P than the soil remaining as macroaggregates, even when expressed on a sand-free basis. These results suggest that the effects of aggregate size on P sorption depend upon the sources of fertilizer phosphate. For P in organic manure, a partial sealing of small aggregates by particulates was proposed as a mechanism to increase P content in large aggregates (Bhatnagar and Miller, 1985). Elliott (1986) postulated element-specific differences in microbial catabolic processes *vs.* extracelluar enzyme activity and its attendant feedback controls to account for this difference.

In summary, soil aggregation influences P status and nutrient uptake by roots. Phosphorus bioavailability probably increases with aggregate size because of decreased P sorption. In contrast, the accessibility of P can be decreased by increasing aggregate size and reduced root growth in large aggregates.

CHAPTER 2 SOIL AGGREGATION AND MICROSTRUCTURE

ABSTRACT

Although highly weathered soils may contain 50% or more amorphous materials estimated by the Rietveld method, the relationship between soil structure and amorphous materials has not been quantified. The structure of the soil influences the retention and transport of solutes, and root penetration. The purposes of this study were to quantify the relationship between soil aggregation and amorphous materials, and the relationship between soil aggregation and pore size distribution. The structure was evaluated by determining aggregate and pore size distribution, and soil amorphous materials were estimated by the Rietveld method. Geometric mean diameter and weighted mean diameter of water-stable aggregates increased with increasing content of soil amorphous materials. A highly negative correlation between aggregate diameter and the ratio of $SiO_2/(Fe_2O_3 + Al_2O_3)$ of the amorphous materials was also found. These soils were characterized with 30- 40 % of total porosity filled with water at 1.5MPa of suction due to the presence of intra-aggregate pores. Existence of such pores (2-3 μm in width) was verified with the aid of a scanning electron microscope. Results indicated an important role of amorphous materials in soil aggregation. The high proportion of intra-aggregate pores in highly aggregated soils may have significant contribution to the retention of nutrients and hazardous solutes.

INTRODUCTION

The mechanisms by which amorphous materials increase soil aggregation and stability have been investigated for several decades. Amorphous material coatings have been found on soil minerals (Tweneboah et al., 1967; Jones and Uehara, 1973; Uehara and Jones, 1974). Uehara and Gillman (1981) pointed out that the cements binding particles of highly weathered soils into laterite blocks were most probably weathering products consisting of a gelatinous mixture of non-crystalline, silica-poor aluminosilicates, free sesquioxides and organic matter while, in arid regions, the cement binding particles in surface crusts was most probably silica. The interaction of the poorly crystalline iron oxide, ferrihydrite, with kaolinite clay was studied as a function of pH (Saleh and Jones, 1984; Yong and Ohtsubo, 1987). At low pH, where the oxides carry sufficient positive charge, they precipitate on clay surfaces. These coatings, once formed, are stable at higher pHs (Goldberg, 1989). Precipitation of oxides at high pH occurs as phases separate from the clays.

Recently clay-organic complexes have received more attention as cementing agents (Tazaki et al., 1989; Bartoli et al., 1992; Gu and Doner, 1993). The cementing materials in sand dunes were characterized as poorly crystalline small particles and non-crystalline gel networks that were composed of aluminosilicates having a high carbon content (Tazaki et al., 1989). Bartoli et al. (1992) found that their results were explained more satisfactorily by the concept of colloidal organo-mineral association than by an organic coating on the surfaces in studies of humic macromolecule effects on surface and colloidal properties of Fe (III) polycations (poorly ordered hydrous iron oxides). Gu and Doner (1993) found that hydroxy-Al polycations effectively screened the surface negative charge on clay colloids and, in addition, acted as bridges between negatively charged colloids and anionic polysaccharides, and thus prevented soil clay dispersion. These studies suggest that negatively charged humic substances may not contribute to stable soil aggregation in the absence of polyvalent cations, whereas the presence of both polyvalent cations and polyanions may be additive in preventing soil clay dispersion. However, these mechanisms may not be applicable to the soils with low clay activity in the tropics where the clay fractions are characterized as Al and Fe, and hydrous oxides, which may possess positive charges, and even net positive charges. It appears that large organic molecules with negative charge can act as a bridge between positively charged particles and amorphous materials.

Many important soil physical properties, especially those pertaining to the retention and transport of solutions, gases, and heat are correlated with soil structure (Danielson and Sutherland, 1986). Soil structure can be measured in many ways, but perhaps it is most meaningfully evaluated through knowledge of the distribution of soil pores. Where the aggregates are fairly distinct, it is sometimes possible to divide pores into two distinguishable size ranges, namely macropores and intra-aggregate pores. The macropores are mostly the inter-aggregate cavities, which serve as the principal avenues for the infiltration and drainage of water, for solute transport, and for aeration. The micropores are the intra-aggregate capillaries responsible for the retention of water and solutes (Hillel, 1982).

Pore size distribution is determined by texture and the structure of the soil. The role of texture becomes less important with increasing structural development. This is especially true in strongly structured Oxisols and Ultisols where moisture release characteristics cannot be predicted by texture alone (Sharma and Uehara, 1968; Tsuji et al., 1975). These soils still contain 20-30% (w/v) water at 1.5MPa (15 bar), or approximately 30-40% of the total porosity filled with water (assuming soil bulk density of 1 and soil particle density of 3). This suggests the significance of intra-aggregate pores in retention of water and solutes in the low clay activity tropical soils.

The exchange of nutrients between the intra-aggregate pores and the inter-aggregate pores may be limited by the diffusion of nutrients. The much slower exchange of isotopic P is caused by access to sites via very restricted pathways and slow diffusion (Nye and Staunton, 1994). Nutrients, such as P, in the intra-aggregate pores may not be immediately available to or not accessible to plants while migration of nutrients into these pores may also be slow. Thus, phosphate diffusion into intra-aggregate pores has been proposed as a mechanism responsible for the slow reactions in soils (Cabrera et al., 1981; Madrid and De Arambarri, 1985; Parfitt et al., 1989; Torrent et al., 1990; Torrent et al., 1992; Nye and Staunton, 1994).

The purposes of this study were to quantify the relationship between aggregation and mineralogy, and the relationship between soil aggregation and pore size distribution.

MATERIALS AND METHODS

Soils

Three soils of the Kapaa, Wahiawa, and Leilehua series in Hawaii were chosen because of their importance in agricultural production and differences in soil aggregation, mineralogical composition, and P fixation. Classifications of these soils are given in Table 2.1. The Kapaa and Wahiawa samples were collected from long-term plots, where ten target P concentrations in solution were maintained from 1971 to 1989 at the Wailua Experiment Station on Kauai, and at the University of Hawaii Poamoho Experiment Station on Oahu, respectively (Rajbhandari, 1991). Soil samples from the surface layer (0-20 cm) with target P concentrations in solution of 0.003, 0.025, 0.1, and 1.6 mg L^{-1} were collected in June, 1995 in the sites. For P levels of 0.003 and 1.6 mg P L^{-1}, three subsamples (2 kg each) from a single plot (only one block) were taken, and for P levels of 0.025 and 0.1 mg P L^{-1}, two subsamples from each plot of two blocks were took. The Leilehua samples from the surface layer (0-20 cm) were collected from the P experiment plots at Waiawa Correctional Facility on Oahu in December, 1993, where a rate of 200 kg P ha^{-1} was applied in October, 1990. One sample from each plot of three blocks and two P treatments (control and P added) were taken.

The subsamples were separately stored in plastic bags, and were air-dried for approximately one week at 25° C in the laboratory and passed through a 6-mm sieve before separating into differing-size aggregates by the dry-sieving method. The soils and their selected sizes of aggregates (4 - 6, 0.5 - 1, and 0.053 - 0.125 mm) were analyzed for organic carbon content using the Walkley-Black procedure (Walkley, 1947; Peech et al., 1947; Greweling and Peech, 1960; Nelson and Sommers, 1982), clay content determined by the hydrometer method (Gee and Bauder, 1986), and soil pH (ratio 5:1 of water to soil).

Nine other Hawaiian soils were also used for measuring the soil aggregate size distribution. These soils were the Kaiwiki, Halii, Kapaa, Makapili, Maolokai, Wahiawa, Haiku, Pulehu, and Waialua soils (Jackman, 1995; Babcock, 1996).

Table 2.1. Soil series and classifications.

Soil series	Classification[†]
Leilehua	clayey, oxidic, isohyperthermic, Typic Kandihumult
Kapaa	v. fine, sesquic, isohyperthermic, Anionic Acrudox
Wahiawa	v. Fine, kaolinitic, isohyperthermic, Rhodic Eutrustox

[†] The soils are classified according to the 1992 revision of Soil Taxonomy (Soil Survey Staff, 1992).

Quantitative Mineralogical and Amorphous Analysis

Clay mineralogy was examined by X-ray diffraction analysis of the selected aggregate sizes (4-6, 0.5-1, and 0.053-0.125 mm) and of the clay fraction for all three soils. The clay-size fraction was separated by ultrasonic dispersion and centrifugation. The aggregate fractions were not separated into clay-size fractions due to the difficulty in soil dispersion with ultrasound. Chemical reagents for soil dispersion were not used because they would dissolve minerals in the soils and lead to overestimates of soil amorphous content. Therefore, "whole soils" for the aggregate fractions (not clay fraction) were used for X-ray diffraction analysis. All the samples were air-dried and ground in an agate mortar and pestle. The samples were then split into two sub-samples. One sub-sample was mixed with 30 % of corrundom SRM 676 spike in the agate mortar (Babcock, 1996). The sub-samples with spike and without spike were packed into zero-background aluminum cavity mounts which accommodate a 2-mm-thick specimen. X-ray diffraction was conducted with a Philips Norelco diffractometer with a cobalt tube operated at 40 kV, 25 mA with an integration time of 4 seconds per step. Intensities were collected at 0.025 degrees 2θ per step for a range of 4 to 80 degrees 2θ.

Quantitative mineralogical analysis of the X-ray diffraction pattern was performed using the SIROQUANT© (Sietronics, Pty. Ltd. 1993) computer program. This program utilizes the Rietveld method to simulate the observed X-ray diffraction pattern and quantify mineral composition of the sample. The pattern is simulated from the structural factors of the mineral by calculating the position and intensity of each peak generated by the diffraction of X-ray.

Amorphous contents in soils can be calculated provided that a highly crystalline "internal standard" is added to the samples prior to X-ray diffraction and Rietveld refinement (Babcock, 1996). In the "internal standard" method of phase analysis, a known weight of a reference phase is added to the mixture. Taylor (1989) described the method of amorphous material calculation. The SIROQUANT© method normalizes all crystalline components to 1, discounting amorphous material content. Therefore, if a crystalline mineral, called a spike, is added to the sample in a precise amount, the amorphous material content can be estimated.

Aggregate Size Distribution

Soil aggregate size distribution was determined by a wet-sieving method described by Gardner (1956) for the three soils used in this experiment and the nine other Hawaiian soils used by Jackman (1994) and Babcock (1996) (the Maile soil not included). Six sieves, 0.1, 0.177, 0.25, 0.42, 0.84 and 2 mm in diameter, were used in this study. They were nested, the largest sieve at the top and the smallest one at the bottom. The soils were wetted by capillary rise without vacuum before sieving.

The wet-sieving was performed in sieving tanks. The nest of sieves was oscillated up and down at 30 cycles per minute for a 30-minute period. At the end of the 30-minute of oscillation, the sieves were removed and allowed to drain. The sieves were dried in an oven at 70°C. The aggregates on each sieve were transferred to aluminum dishes and dried at 105°C for 24 hours.

Soil retained on each sieve was expressed as a percentage of the whole soil. Percentages were calculated using the oven-dry weight of the sample as the basis for calculations. The mean weighted diameter (MWD) and geometric mean diameter (GMD) described by Van Bavel (1949) and Mazurak (1950), respectively, were calculated for each soil as follows:

For GMD

$$GMD = \exp(\sum_{i=1}^{n} w_i \log \overline{x_i})$$

For MWD

$$MWD = \sum_{i=1}^{n} w_i \overline{x_i}$$

where $\overline{x}_i$ is the mean diameter (i.e. midpoint) of each size fraction, and w_i is the proportion of the total sample weight occurring in the corresponding size fraction, n is the number of size fractions.

The use of the geometric mean in aggregate size analysis was due to the empirical finding that many aggregate size distributions conform satisfactorily to the log normal law. Kolmogorov-Smirnov tests indicated that aggregate size distributions in this experiment were approximately log normal. It should be noted that the geometric mean is the median of the lognormal distribution.

The MWD was considered in this experiment because it is easily calculated and visualized by most individuals. A high correlation between MWD and GMD was reported (Schaller and Stockinger, 1953). Kemper and Rosenau (1986) state that both the MWD and GMD can be used to represent aggregate size distribution for statistical analysis.

Associations of MWD and GMD with soil amorphous materials were measured using the Pearson correlation coefficient. For the nine other Hawaiian soils, data of amorphous materials were from Babcock (1996).

Pore Size Distribution

Water desorption curves of the soils were used to estimate the size distribution of soil pores. The calculation of pore size is based on the assumption that the pores are of capillary-tube shape and that the contact angle of water to soil is zero (Danielson and Sutherland, 1986). The diameter (d_p) in μm of the largest water-filled pore at each equilibrium can be expressed as

$$d_p = 4\,\sigma \times 10^5/(\rho_m\, g\, h)$$

where σ and ρ_m are surface tension (J m^{-2}) and density (Mg m^{-3}) of water, g is the gravitational acceleration (m s^{-2}), and h is the matric suction (centimeters of water). The fraction of total pore space filled with water was plotted as a function of pore diameter to express the pore-size distribution.

The water desorption curves of the whole soil (< 2 mm) and selected aggregate fractions (4 -6, 0.5 -1, and 0.053 - 0.125 mm) were carried out in a range of 4.5×10^3 - 1.5×10^6 Pa using a pressure plate apparatus. Samples were saturated in a vacuumized desiccator with the soils wetted from the bottom of the ring to the top. The soils were then equilibrated with water for at least 24 hours.

Scanning Electron Microscope

A scanning electron microscope (SEM) was used to examine intrapore features of individual aggregates at a high magnification. For scanning electron microscopy, air-dried, freshly fractured aggregates with sizes of 4-6, 2-4, and 1-2 mm were attached to aluminum support stubs, silver-coated, and gold-coated by vacuum evaporation.

Statistical Analysis

Pearson correlation coefficients were used as a measure of the linear association between two measured variables. The standard deviation was used to estimate the variation of a treatment while the standard error was used for comparing two treatments.

All statistical analysis was performed with S-PLUS (Statistical Science, 1995).

RESULTS AND DISCUSSION

Characteristics of whole soils and aggregates

Selected physical, chemical and mineralogical properties of the Kapaa, Leilehua, and Wahiawa soils are shown in Table 2.2. The whole soils are characterized by high clay contents with the Kapaa soil containing 500 g kg^{-1}, the Leilehua soil 790 g kg^{-1}, and the Wahiawa soil 910 g kg^{-1}. The pH values were 4.61, 5.21, and 6.01 for the Leilehua, Kapaa, and Wahiawa soils, respectively.

Table 2.2. Selected soil characteristics of the Kapaa, Wahiawa, and Leilehua soils.

Phase[†]	Kapaa Series				Wahiawa Series				Leilehua Series			
	Whole[‡]	4-6	0.5-1	0.053-0.125	Whole	4-6	0.5-1	0.053-0.125	Whole	4-6	0.5-1	0.053-0.125
Kaolin	17	56	40	51	530	349	456	530	287	190	198	199
Gibbsite	115	315	237	216	13	15	23	10	12	25	19	24
Goethite	211	158	163	156	--	--	--	--	131	81	98	89
Anatase	43	38	61	41	--	--	--	--	102	91	106	94
Hematite	24	36	27	51	95	156	97	102	62	54	56	52
Magnetite	21	17	12	14	02	1	1	0	--	--	--	--
Quartz	12	18	19	28	11	8	12	13	22	45	47	41
Ilmenite	3	8	4	0	--	--	--	--	9	70	66	56
Illite	--	--	--	--	115	170	130	99	--	--	--	--
Rutile	--	--	--	--	--	--	--	--	32	40	42	26
Amorphous[§]	555	354	439	444	235	302	280	247	343	403	368	419
O. C.	71	64	75	84	24	27	28	49	57	61	65	86
Clay	500	430	500	540	910	910	910	910	790	780	810	830
pH	5.2	5.3	5.2	5.3	6.0	6.0	6.0	6.0	4.6	4.7	4.6	4.6
GMD[¶]	1.8	--	--	--	0.4	--	--	--	1.0	--	--	--
MWD[#]	2.3	--	--	--	0.7	--	--	--	1.7	--	--	--

[†] The values for minerals, amorphous materials, clay, and O.C. represent g kg^{-1} on the basis of oven-dried soil.

[‡] Whole, 4-6, 0.5-1, and 0.053-0.125 represent whole soil, and aggregate fractions with sizes of 4-6, 0.5-1, 0.053-0.125 mm, respectively.

[§] Amorphous materials in the soils estimated by the Rietveld method.

[¶] GMD: geometric mean diameter (mm).

[#] MWD: mean weighted diameter (mm).

The amorphous material contents estimated with the Rietveld method in the soils were very high with the Kapaa soil 555 g kg^{-1}, the Wahiawa soil 235 g kg^{-1}, the Leilehua soil 343 g kg^{-1}. The organic carbon content of the Kapaa soils was greater than the Leilehua soil. The Wahiawa soil had the lowest value. The range in soil organic carbon content of the soils studied is consistent with the change in amorphous material. The soil amorphous materials protect the soil organic matter from decomposition, probably, due to the formation of organic complexes with Si, Al, and/or Fe.

Relationship between amorphous materials and soil aggregation

The water-stable aggregate sizes of the three soils were different (Figure 2.1). Aggregates with mean diameter greater than 1.4, 1.0, and 0.3 mm accounted for fifty percent of total soil mass for the Kapaa, Leilehua, and Wahiawa soils, respectively. The GMD value of the Kapaa soil was four times the value of the Wahiawa soil, and the GMD of the Leilehua soil was between the Kapaa and Wahiawa soils (Table 2.2). The change in water-stable aggregate size was consistent with the change in soil mineralogy (Table 2.2, Figure 2.2). Gibbsite, goethite, and anatase were the predominant minerals in the Kapaa soil which also contained a high content of amorphous materials, while kaolinite, illite, and hematite were predominant minerals in the Wahiawa soil which contained a low content of amorphous materials. The values of GMD and MWD seemed to relate to amorphous materials (Figure 2.2). The diameters (GMD/MWD) increased with increasing amorphous material content. Goldberg (1989) concluded that Al and Fe

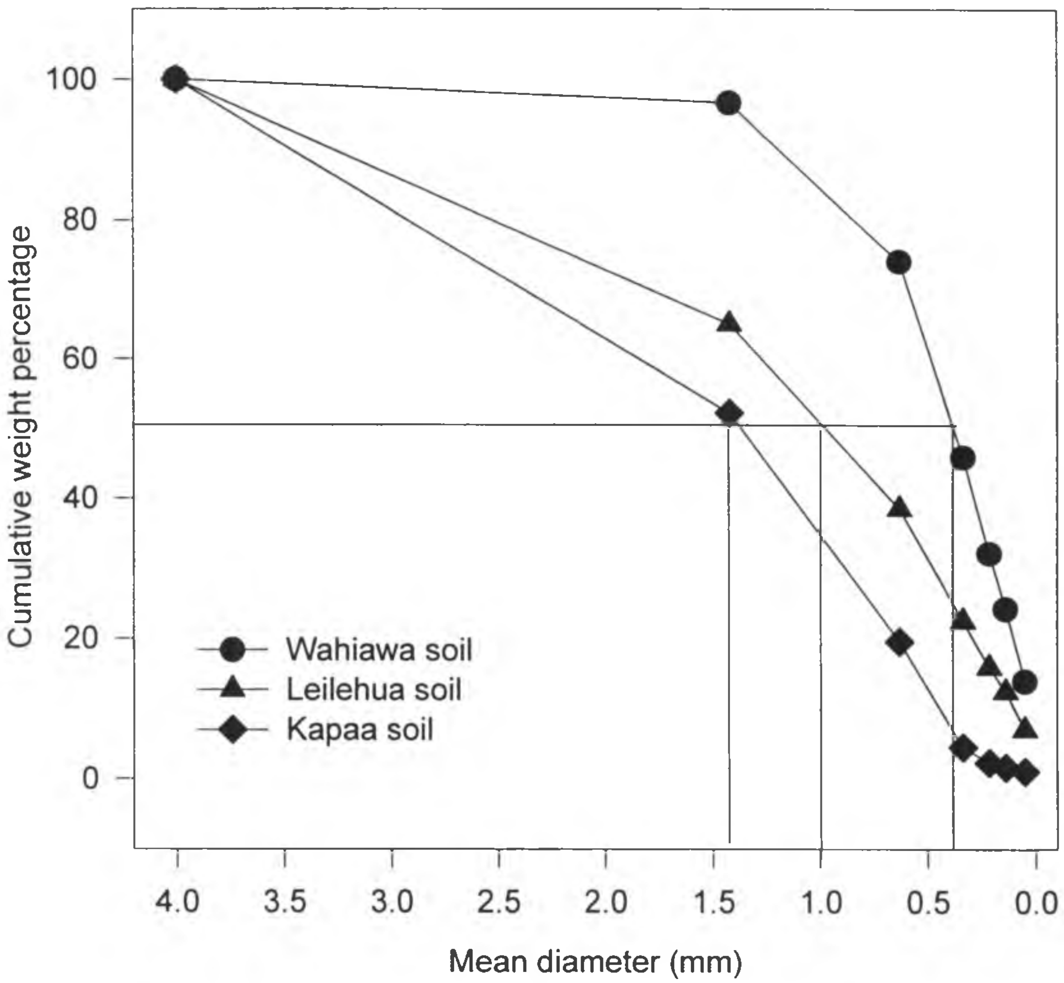

Figure 2.1. Water stable aggregate size distribution of the three soils.

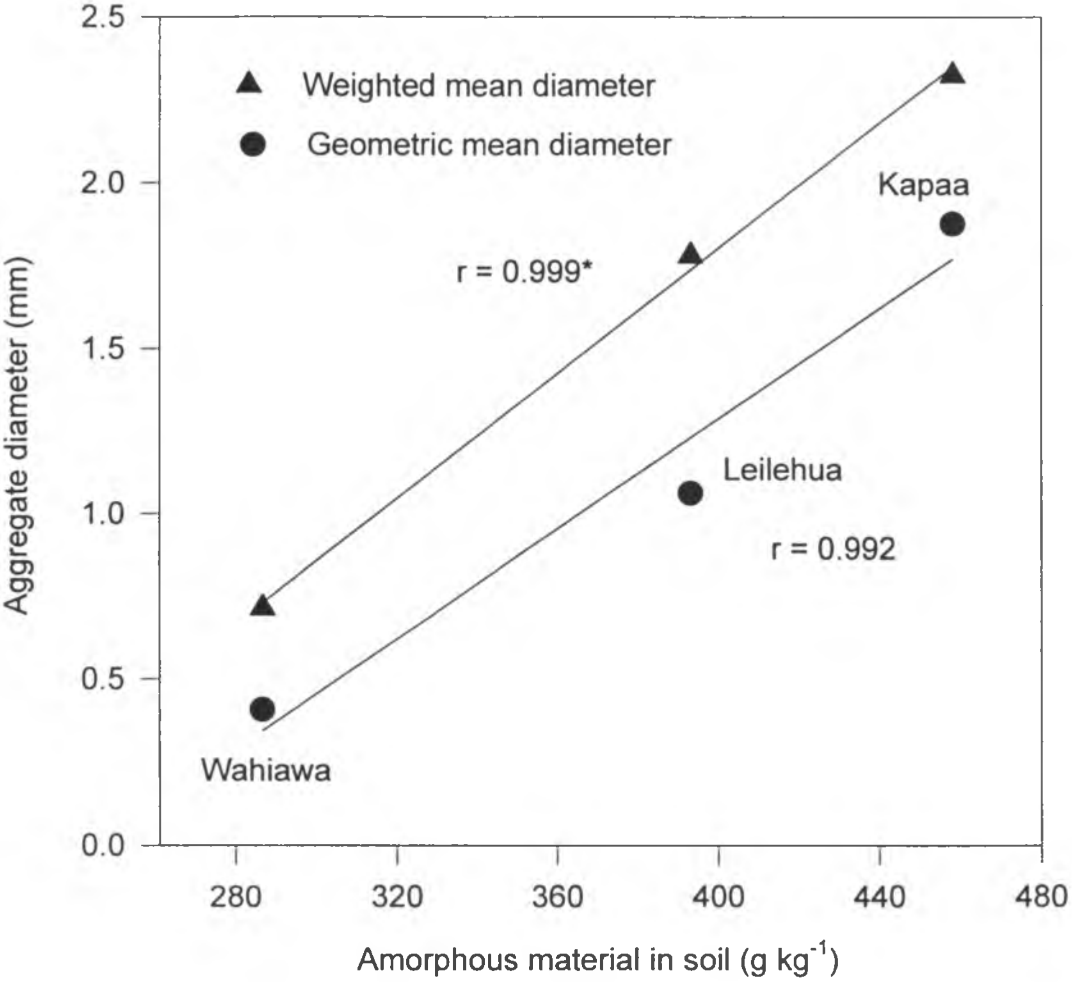

Figure 2.2. The relationship between amorphous materials estimated by the Rietveld method and aggregate size for the three soils.

oxides stabilized clay minerals by decreasing the critical coagulation concentration, clay dispersion, water uptake, and clay swelling and by increasing microaggregation.

The ability to measure the amount and composition of amorphous materials as well as crystalline minerals in soils gives an insight into the roles of these components in influencing soil aggregation as well as soil behavior and performance. Recently Babcock (1996) developed a methodology to determine crystalline phase concentrations and total amorphous materials by the Rietveld method. The oxide composition of the amorphous materials was estimated by the difference in the oxides measured by x-ray fluorescence and by the Rietveld method. For Hawaiian soils with a wide range in mineralogy and P sorption, the contents of amorphous materials in clay fractions found by the Rietveld method were much greater than by acid ammonium oxalate extraction (Babcock, 1996). Such difference is possible because the two methods report different portions of the clay fractions. The major disadvantage of a chemical dissolution technique is that it is difficult to assess what portion of the soil is extracted because of nonspecific dissolution of soil components. The oxalate extractant removes some short range ordered oxides and hydroxides of Al, Fe, and Mn (Schwertman 1973; McKeague et al., 1971). The severity of dissolution of some crystalline minerals increases with a decease in particle size (McKeague et al., 1971).

Soil aggregate size, expressed by GMD and MWD, was highly correlated with the contents of amorphous materials estimated with both the Rietveld method and the oxalate extraction. However, GMD and MWD were better correlated with the content of amorphous materials estimated with the Rietveld method than with the oxalate extraction (Figure 2.3-2.4); the difference would be even greater if the one extreme observation were not included. The relationships of aggregate size to the amorphous aluminum and iron oxides in the soils, and the ratio of $SiO_2/(Al_2O_3 + Fe_2O_3)$ in the amorphous materials are shown in Figure 2.5-2.6. These results support the linear associations of the aggregate size with the amorphous materials estimated by the Rietveld method for the other three Hawaiian soils (Figure 2.2).

The organo-amorphous materials with negative charge could be efficient cements in positively charged tropical soils if electrostatic bonds are the main inter-aggregate bonds. Negatively charged organo-mineral associations were reported when synthetic humic macromolecules were adsorbed on poorly ordered ferrihydrite (Bartoli et al., 1992). On the other hand, the large amount of amorphous material found in the tropical soils, using the Rietveld method, suggests a possibility of physically occluding crystalline particles through dehydration of amorphous materials. Some non-crystalline materials dehydrate irreversibly into aggregates of silt, sand and gravel size as in the Hydrudand (Soil Taxonomy, 1975).

Mineralogical Composition among Aggregates

The mineralogical types among aggregates for all three soils were quite similar. The change in mineral content, however, varied with the soils. Aggregate size fractions contained a similar distribution of minerals for the Leilehua soil, which were

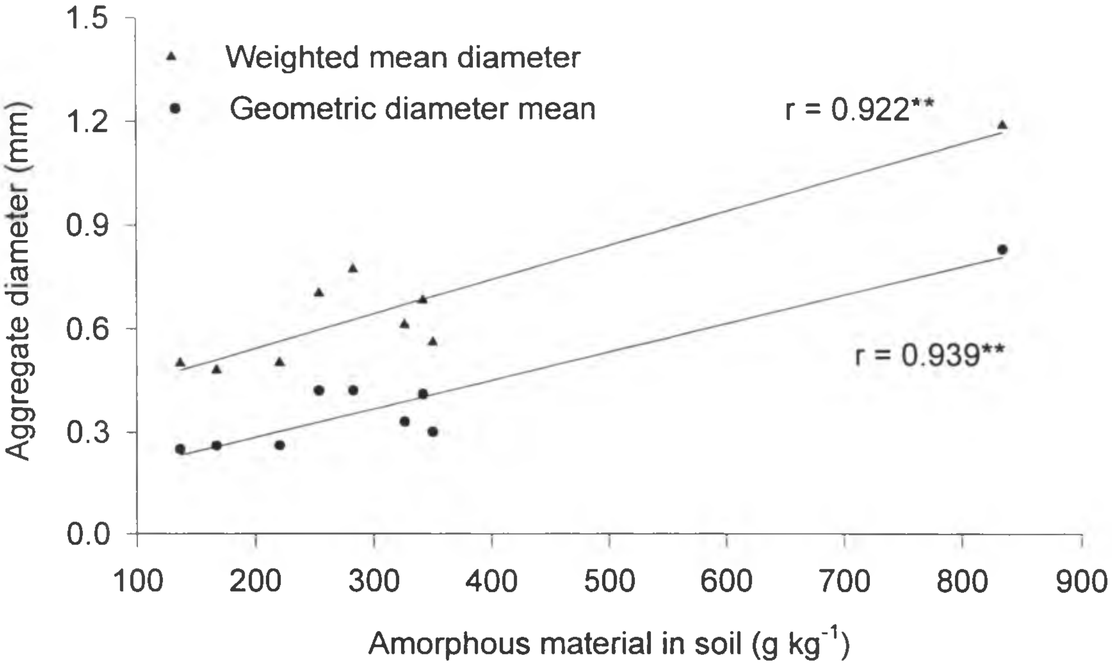

Figure 2.3. Relationship between amorphous material determined by the Rietveld method and aggregate diameter for nine soils. Data of amorphous materials were from Babcock (1996).

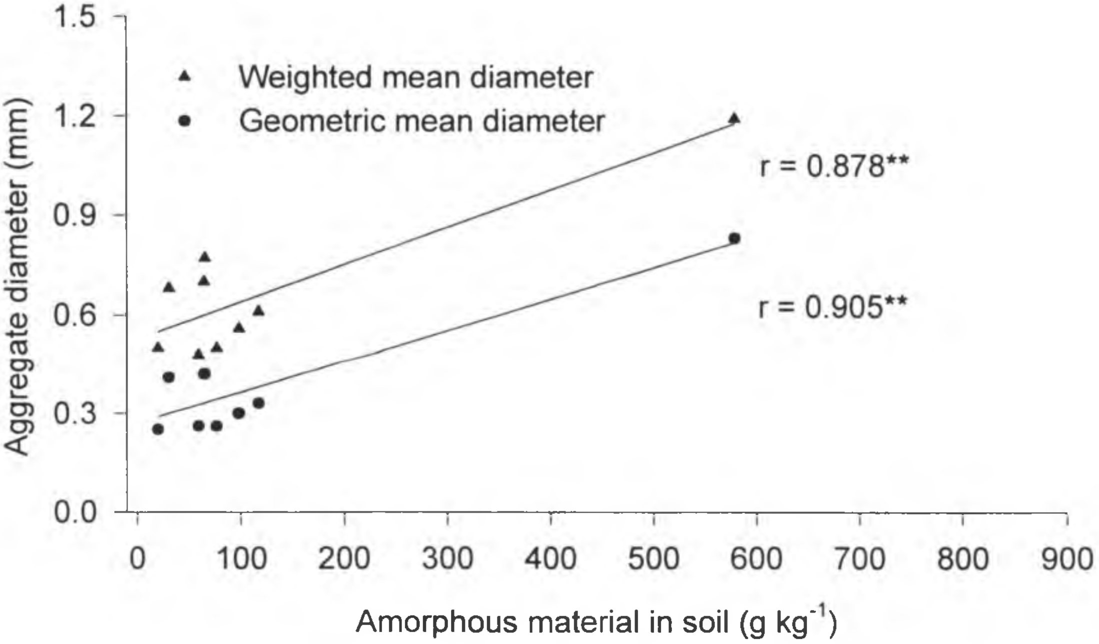

Figure 2.4. Relationship between amorphous materials determined by the oxalate extraction and aggregate diameter for nine soils. Data of amorphous materials were from Babcock (1996).

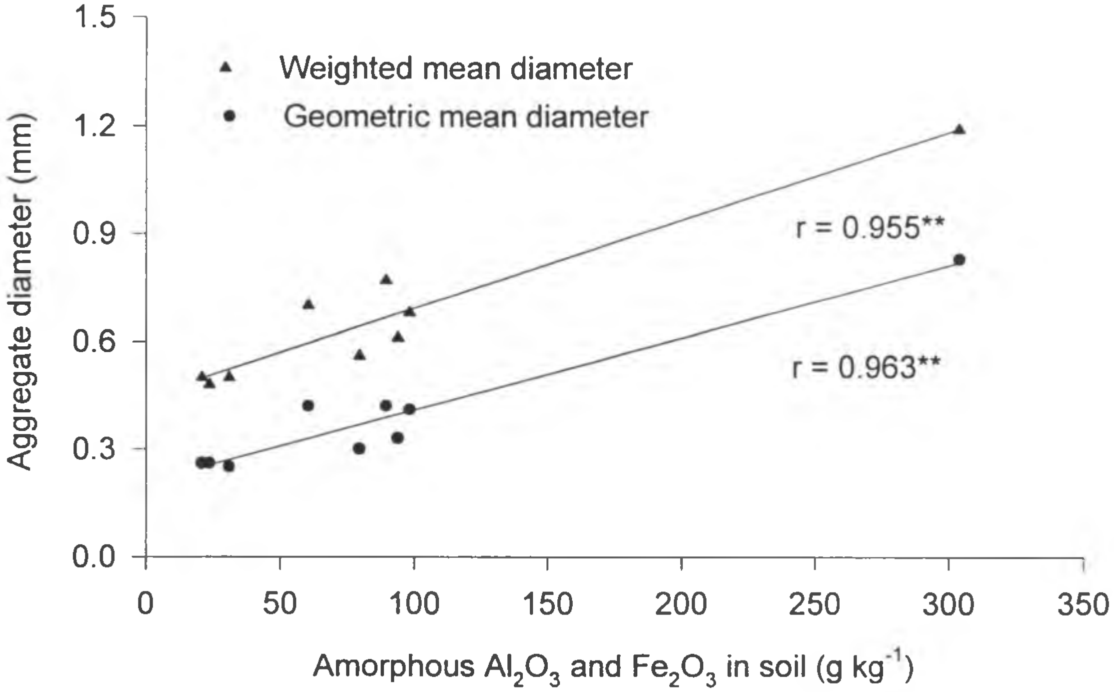

Figure 2.5. Relationship between amorphous Al_2O_3 and Fe_2O_3 and aggregate diameter for nine soils. Data of amorphous materials were from Babcock (1996).

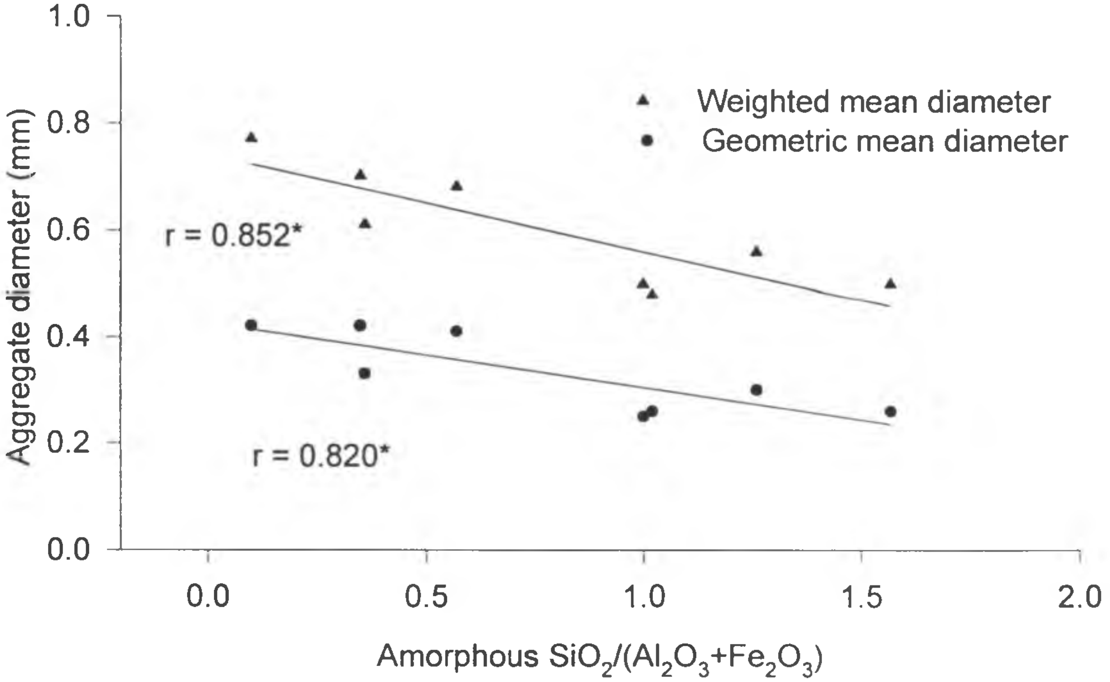

Figure 2.6. Relationship between amorphous $SiO_2/(Al_2O_3+Fe_2O_3)$ and aggregate diameter for nine soils. Data of amorphous materials were from Babcock (1996).

predominately kaolinite, with goethite and hematite. In contrast, gibbsite in the large aggregates (4-6 mm) was greater than in small aggregate fractions (0.5-1, and 0.053-0.125 mm) of the Kapaa soil. Note that goethite in clay fraction was greater than gibbsite while goethite in aggregates (aggregates were not separated into clay fractions) was less than gibbsite. For the Wahiawa soil, the content of hematite and illite decreased with decrease in aggregate size while the content of kaolinite increased with decrease in aggregate size.

It is difficult to interpret the effect of amorphous materials in the aggregates, although amorphous materials are important for soil aggregation and aggregate stability. With increased aggregate size, the content of amorphous materials appeared to decrease in the Kapaa soil, while amorphous materials appeared to increase in the Wahiawa soil. The low content of amorphous materials in the large aggregates (4-6 mm) of the Kapaa soil may be related to the crystallization of the minerals, such as gibbsite and goethite. The Leilehua soils appeared to contain similar amounts of amorphous materials for all the aggregate size fractions.

Pore Size Distribution of Soils and Aggregates

Pore size distribution strongly affects the pore surface area which, to a large extent, controls the retention of most nutrients in soils. Phosphate diffusion into the intra-aggregate pores may be affected by pore size distribution, pore geometry, and connection of pores, which, in turn, influence long-term P management and prediction of fertilization needs.

Plots of the volume fraction of total pore volume filled with water (%) vs. pore diameter for the Leilehua, Kapaa, and Wahiawa soils are shown in Figure 2.7-2.10. These plots were developed from the corresponding soil-water characteristic data for each sample. The volume fraction of total pore volume for any given diameter d_0 represents the fraction of pore volume occupied by pores with diameter $\leq d_0$. Thus these plots are also cumulative pore-size distribution curves describing soil porosity.

For the Leilehua soil, the volume fraction of total pore volume for any given pore diameter was greater than that for the Kapaa soil (Figure 2.7), although geometric means of pore size for both the soils were similar (Table 2.3). Note there were 34%, 34%, and 44% of total pore volume at 1.5 MPa of suction for the Kapaa, Wahiawa, and Leilehua soils, respectively (Figure 2.7). Existence of such pores was demonstrated with the aid of a scanning electron microscope (Figure 2.11). The surfaces of the aggregates consisted of voids with diameters of a few micrometers. Tsuji et al. (1975) also showed that these voids were obvious in soils with kaolinitic and oxidic mineralogy, but were not evident in soils of montmorillonitic or amorphous oxide composition. Reactions of P with these soils are likely controlled by P diffusion into these pores.

Geometric mean diameters of pores (calculated only for pore size $\leq 57\ \mu$) were greater for the small aggregate fraction (0.053 - 0.125 mm) in the Wahiawa and Leilehua soils than for the large aggregate fractions (4 - 6, 0.5 - 1 mm) (Table 2.3), indicating an

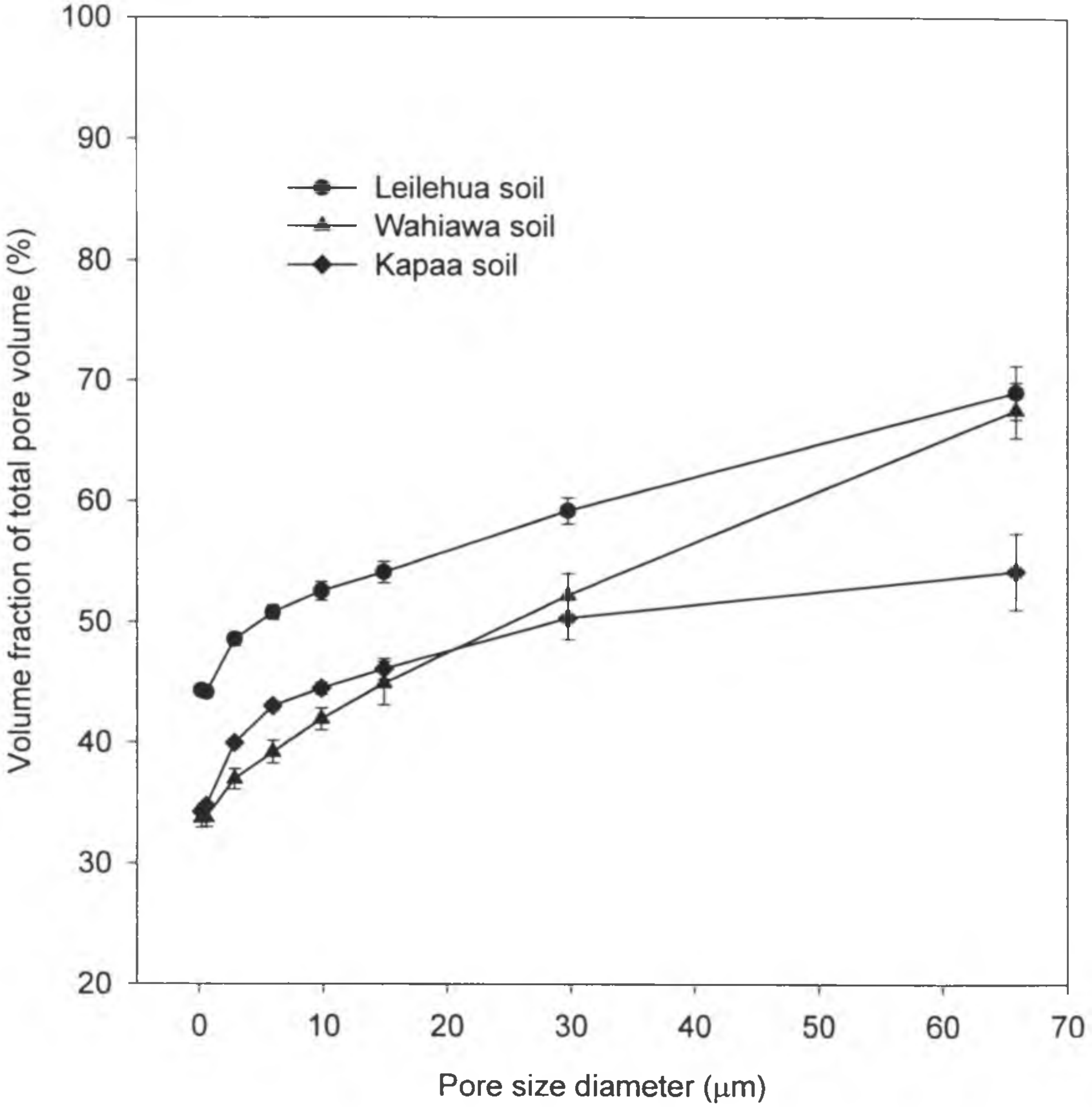

Figure 2.7. Pore size distribution for the whole soils (diameter < 2 mm) Bars represent one standard deviation. Symbol sizes may exceed error bars in some cases.

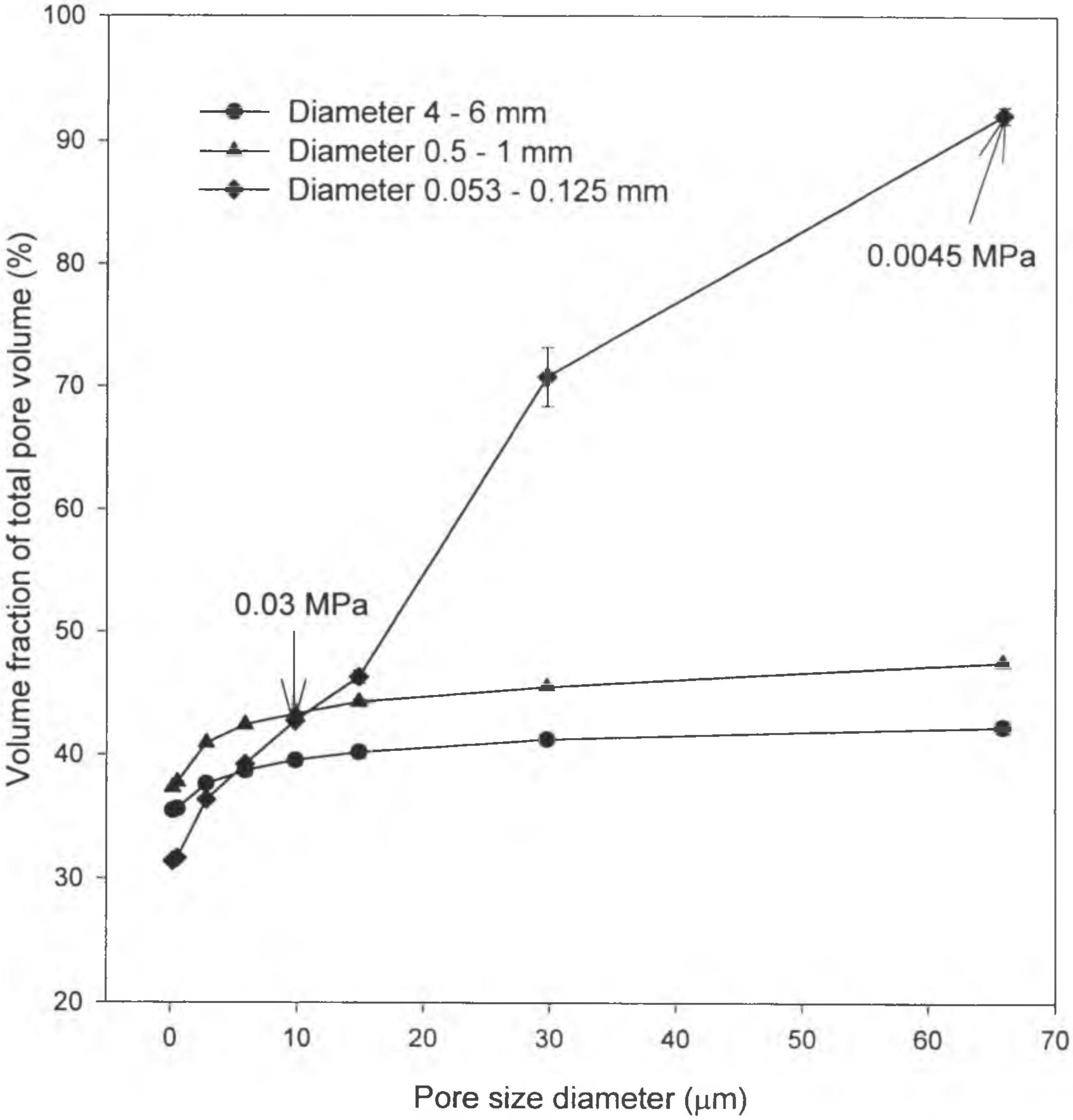

Figure 2.8. Pore size distribution of aggregate fractions for the Leilehua soil. Error bars represent one standard deviation. Symbol sizes may exceed error bars in some cases.

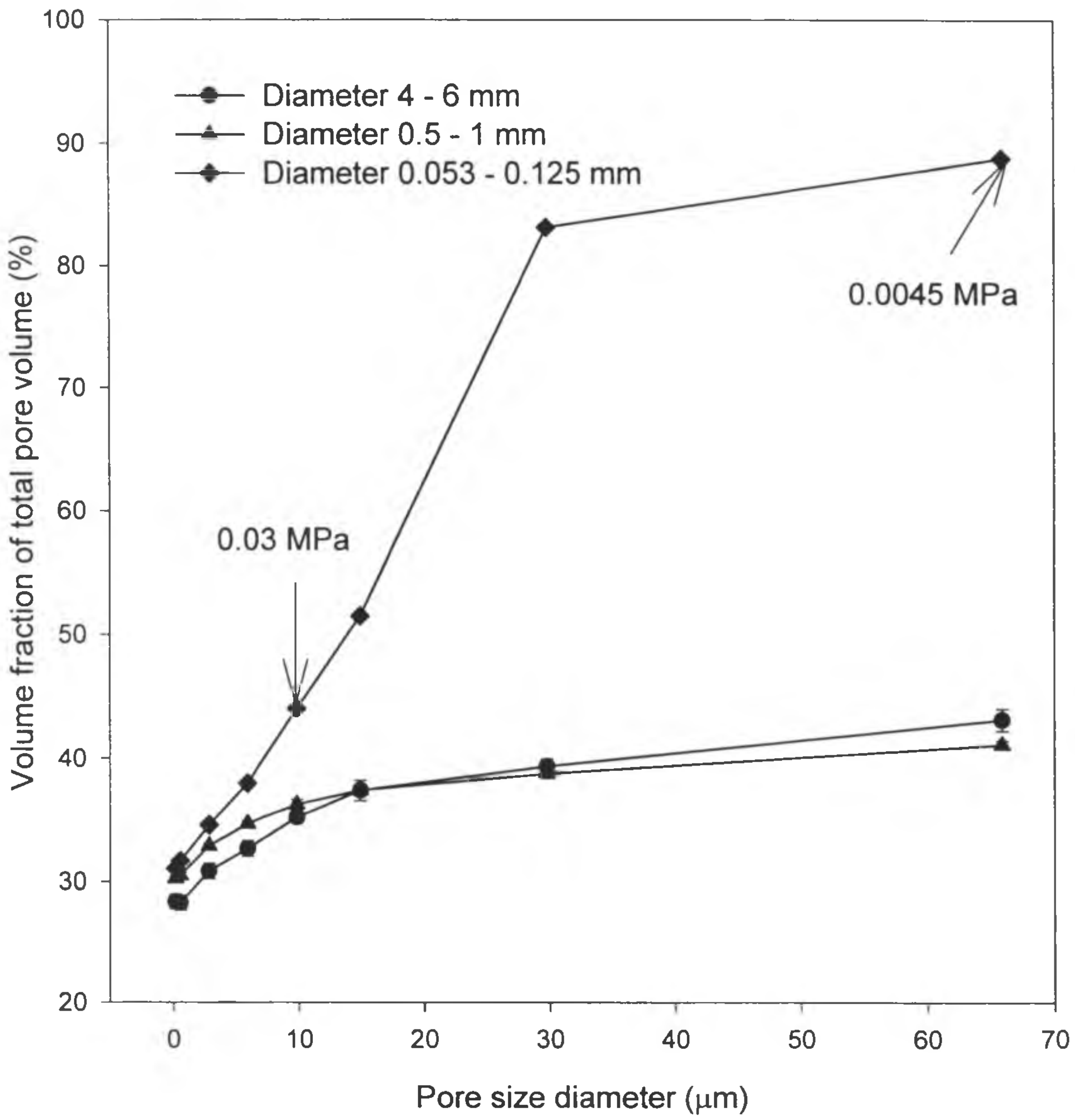

Figure 2.9. Pore size distribution of aggregate fractions for the Wahiawa soil. Error bars represent one standard deviation. Symbol sizes may exceed error bars in some cases.

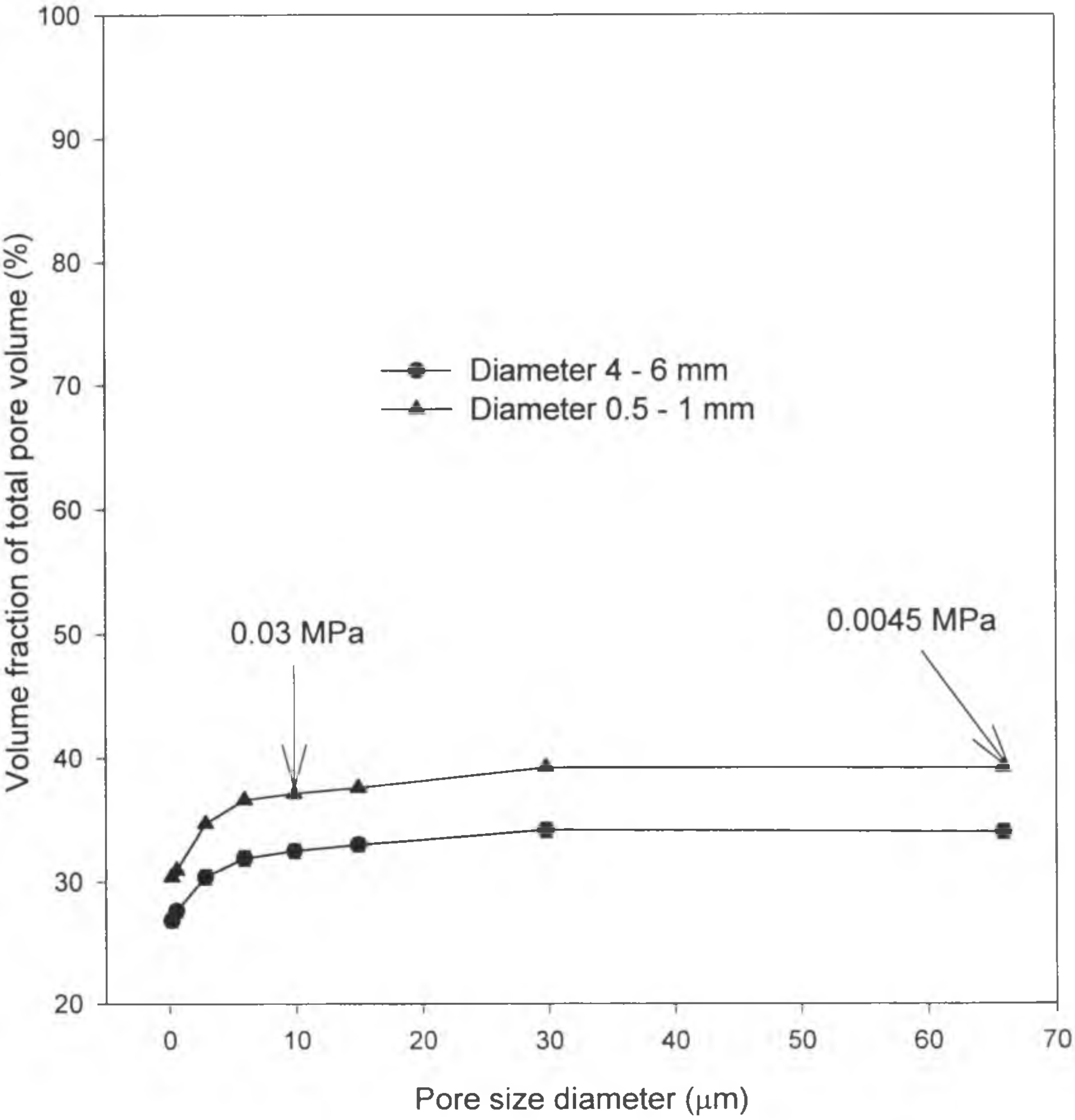

Figure 2.10. Pore size distribution of aggregate fractions for the Kapaa soil. Error bars represent one standard deviation. Symbol sizes may exceed error bars in some cases.

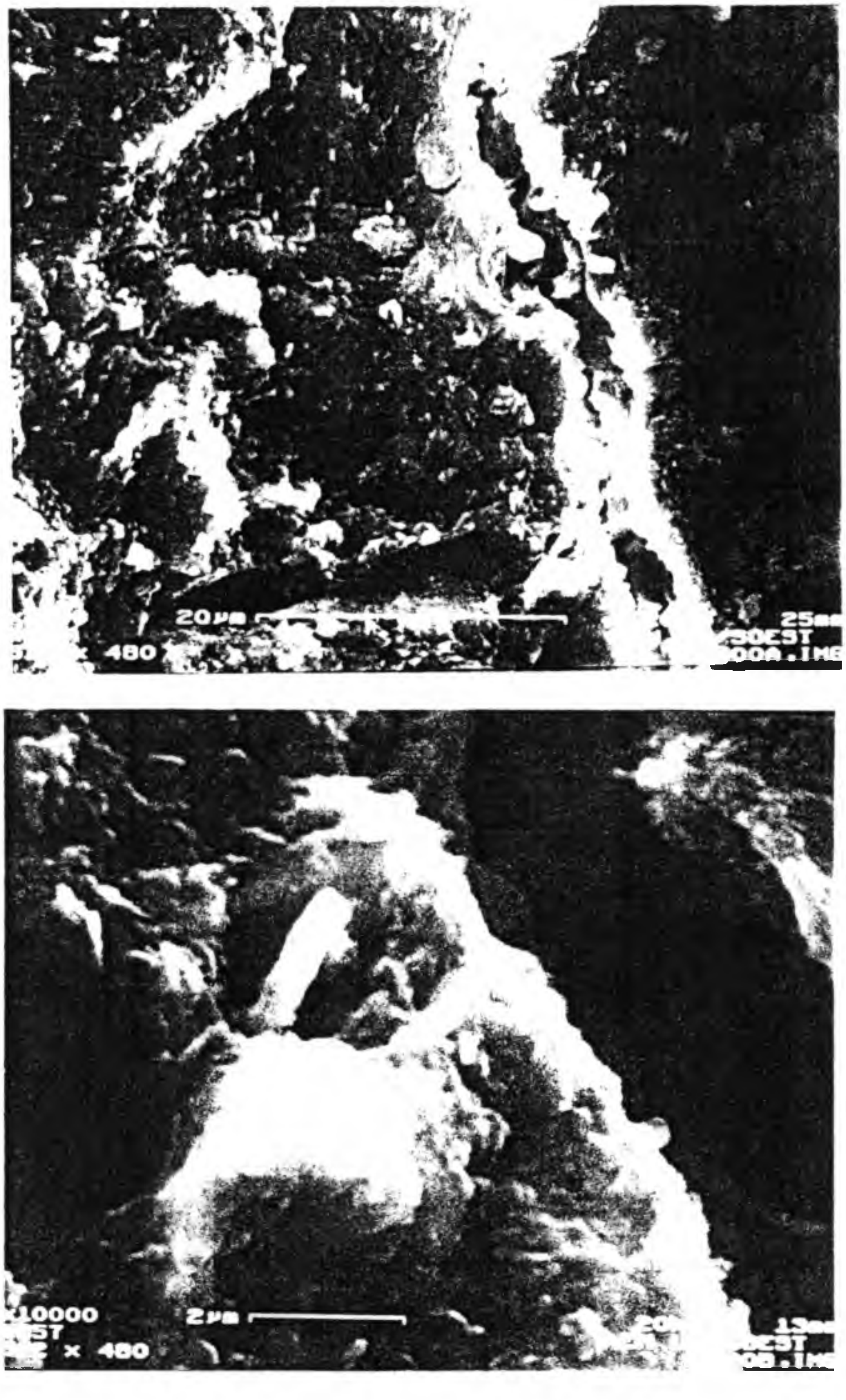

Figure 2.11. Microstructure in aggregates (2 - 4 mm) on the Leilehua soil with scanning electron microscope.

important role of soil aggregation in determining pore size distribution. The difference in geometric diameter of pores was mainly due to the difference in pore size (inter-aggregate pores) distribution at suction between 0.0045 and 0.03 MPa (Figure 2.8-2.9). There was small difference in pore size distribution between 0.03 - 1.5 MPa among aggregate fractions compared to the pore size distribution between 0.0045 - 0.03 MPa in the Leilehua and Wahiawa soils. Thus soil aggregation or aggregate size has more influence on inter-aggregate pore distribution than on intra-aggregate pore distribution. However, aggregate size will affect exchange of water and solute between intra-aggregate pores and inter-aggregate pores.

In addition, there was little difference in pore size distribution between aggregate fraction 0.5 - 1 mm and aggregate fraction 4-6 mm for all three soils.

Table 2.3. Geometric mean diameters (μm) of pore size for the soils and their aggregate sizes.

Soil	Whole	4 - 6 mm	0.5 - 1 mm	0.053 - 0.125 mm
Leilehua	1.02	0.65	0.68	4.39
Wahiawa	1.73	0.93	0.79	3.39
Kapaa	0.93	0.71	0.70	nd[†]

[†] nd: not determined.

CONCLUSIONS

Positive correlations between the geometric mean diameter and weighted mean diameter of water-stable aggregates and the content of soil amorphous materials estimated by the Rietveld method were detected in the Oxisols and Ultisols from Hawaii, suggesting that amorphous materials influence soil aggregation. Other factors that influence soil aggregation may be the ratio of $SiO_2/(Al_2O_3 + Fe_2O_3)$ in the amorphous materials, organic carbon, and crystalline minerals in the soils.

The high fraction of total porosity filled with water at 1.5MPa of suction in the Leilehua, Kapaa, and Wahiawa soil was attributed to the presence of intra-aggregate pores. The existence of such pores 2 - 3 µm in width was verified with the aid of a scanning electron microscope for the Leilehua soil. The intra-aggregate pores of the other Hawaiian soils were described by Tsuji et al. (1975). The significance of the intra-aggregate pores may lie in increases in the soil surface area, thus in water and nutrient retention. The study of retention and transport of nutrients and hazardous solutes in highly aggregates soils could improve nutrient management and protect our environment.

CHAPTER 3

CHANGES IN EXTRACTABLE P WITH AGGREGATE SIZE

ABSTRACT

Phosphorus (P) is one of limited factors for crop production in tropics. The diagnosis and recommendation of nutrient P continues their performances with low precision and high uncertainty. A recent study suggests that soil aggregation may affect P measurement and P availability in the Haiku soil in Hawaii. The objective of this study was to determine the distribution of extractable P among aggregates as related to aggregate size. Three Hawaiian soils (the Kapaa, Wahiawa, and Leilehua series) were sampled from long-term field plots. For each soil, eight aggregate size fractions of < 0.053, 0.053-0.125, 0.125-0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, and 4-6 mm were obtained by the dry-sieving method. For the Kapaa and Leilehua soils, sodium bicarbonate extractable P increased up to 5-fold with decreasing aggregate size when P had been added to soils. The extractable P did not increase with decreasing aggregate size on all soils where no P had been applied and even where P had been applied to the Wahiawa soil. Organic P in aggregates did not change with aggregate size in either the control or P-added treatments on the Leilehua soil. The differing outer surface area of aggregates alone did not explain the change in extractable P with aggregate size. *Effective mass*, an estimated proportion of the total soil mass at a given depth of P diffusion into aggregates, was used to estimate the initially sorbed P and diffusion of sorbed P into aggregates. The change in extractable P in the Leilehua and Kapaa soils was successfully predicted from

the outer surface area of aggregates, effective mass, and aggregate diameter. The lack of a relationship between extractable P and aggregate size in the Wahiawa soil may be related to the low aggregate stability of the Wahiawa soil compared to the Kapaa and Leilehua soils. The change in extractable P with aggregate size suggests that soil aggregation may affect P sorption and P availability.

INTRODUCTION

Soils contain three sizes of pores through which ions move to plant roots (Vaidyanathan and Talibudeen, 1968): (1) inter-aggregate pores, which carry the main body of ions at water content above field capacity; (2) large intra-aggregate pores, which become important in ion-transport when the thickness of water films in inter-aggregate approaches the diameter of intra-aggregate spaces; and (3) smaller intra-aggregate pores, which do not permit ion transport to roots directly. A high portion of intra-aggregate pores (30-40% of total pore volume) at 1.5MPa of suction was reported in highly aggregated Oxisols, and Ultisols (Tsuji, et al., 1975; Chapter 2). Little, however, is known about retention and availability of nutrients in these pores. Measurements of the rates at which soil P is released into the soil solution and of isotopic exchange between soil P and that in solution suggest that most soil P is associated with intra-aggregate pores in which the distribution between larger and smaller pores depends on the reaction time of P with soils (Talibudeen, 1958). Phosphate associated with the surfaces of inter-aggregate pores (and possibly some of the larger continuous intra-aggregate pores) moves

100 times faster than P in intra-aggregates and is mainly responsible for P supply to roots via water in the inter-aggregate space (Vaidyanathan and Talibudeen, 1968). Thus, P in intra-aggregate pores may help to maintain the concentration of phosphate in inter-aggregate pores.

Although aggregation had little influence on the fraction of intra-aggregate pores in aggregate fractions (Chapter 2), it decreased the outer surface area of aggregates, and the accessibility of water and solutes to intra-aggregate pores. It is hypothesized that sorption of added P is governed by the outer surface area since P is strongly sorbed by aggregates. Sorption of added P will, therefore, be greater in small aggregates than in large aggregates after P is applied to a highly aggregated soil and the P-added soil is subsequently separated into differing aggregate fractions. With time when P diffuses into and among aggregates, or in less structured soils, the change in added P with aggregate size should diminish. Distribution of extractable P among aggregates may, however, be related to sorption of added P and the effects of aggregate size and stability on P extractions from aggregates. Extractable P from small aggregates should be greater than from large stable aggregates by decreasing accessibility of extractants to P within the larger aggregates if the total P among aggregates is the same. The purpose of this study was to evaluate the effects of soil aggregate size on extractable P measurement and P supply to plants.

MATERIALS AND METHODS

Soils

The soils used in this experiment and their preparations were the same as in Chapter 2. The air-dried soils (< 6 mm) were sieved into eight aggregate fractions with sieve openings < 0.053, 0.053-0.125, 0.125-0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, and 4-6 mm, shaking the sieve for 15 minutes by hand. The mean diameter (d) of each size fraction was calculated on a volume-weighted basis from the formula (Addiscott et al., 1983)

$$d = \left[\frac{(d_2^4 - d_1^4)}{4(d_2 - d_1)}\right]^{1/3} \qquad (3.1)$$

where d_2 and d_1 are the upper and lower extremes of the diameter range. This was obtained by finding the area under the curve $v=d^3$ between d_1 and d_2 and dividing it by (d_2-d_1). The corresponding volume-weighted mean diameters (VWMD) were 0.033, 0.094, 0.194, 0.388, 0.777, 1.554, 3.107, and 5.066 mm.

Assuming that aggregates were approximately spheres and that bulk density was 1, the outer surface area of aggregates was calculated on the volume-weighted mean diameter:

$$SA = 6/(\rho d) \qquad (3.2)$$

where ρ is the aggregate bulk density, and d is the volume-weighted mean diameter estimated from equation (3.1).

Duplicate samples of each aggregate fraction on the Leilehua soil were extracted with 0.5 *M* $NaHCO_3$ (Olsen et al., 1954) and with 0.1 *M* NaOH (McLaughlin et al., 1977), respectively. The 0.5 *M* $NaHCO_3$ extractable P was used for assessing soil available P while the 0.1 *M* NaOH extractable P measured the P fraction due to sorption reactions and some organic P. The total P from the 0.1 *M* NaOH extract was determined after wet digestion with perchloric acid of an aliquot of the suspension (Olsen and Sommers, 1982). Inorganic P in both 0.5 *M* $NaHCO_3$ and 0.1 *M* NaOH extracts was directly measured immediately after extraction to reduce decomposition of organic P in the extracts. The organic P in 0.1 *M* NaOH suspensions was estimated as the difference between the total P and inorganic P in 0.1 *M* NaOH extracts. Only inorganic P extracted by 0.5 *M* $NaHCO_3$ was determined on the Kapaa and Wahiawa soils. Duplicate samples were also used for these soils. Phosphorus in extracts was determined by the colormetric method (Murphy and Riley, 1962; Watanabe and Olsen, 1965).

An incubation study was conducted to determine the recovery of added P by 0.1*M* NaOH from 1-2, 2-4, and 4-6 mm aggregates of the Leilehua soil. Phosphorus levels of 0, 200, 400, 800 mg P kg^{-1} were separately added to 1-2, 2-4, and 4-6 mm aggregates, then incubated for 30 days. The P levels were replicated three times. The deionized water was added to the samples when they dried. After incubation, 0.1 *M* NaOH extractable P in aggregates were determined. The recovery of added P was calculated as the ratio of 0.1*M* NaOH-extractable P to added P.

Effective Mass

Evidence suggests that initially sorbed P in soils probably remains on the outer surface of aggregates (Gunary et al., 1964, Willet et al., 1988, Linquist et al., 1997). Thus P sorption capacity by varying-size aggregates of a given soil should be controlled by the outer surface area of aggregates. After initial sorption, further distribution of the sorbed P may occur through P diffusion into and among aggregates. Phosphorus diffusion into aggregates is possible because of the high proportion of intra-aggregate pores found in Oxisols and Ultisols (Sharma and Uehara, 1968; Tsuji et al., 1975; Chapter 2). The depth of diffusion of added P into aggregates may be related to the amount of and availability of sorbed P in aggregates. The distribution of added P in aggregates probably influences P uptake by affecting accessibility of plant roots to P in aggregates. Linquist et al. (1997) related *reactive mass* to sorption of added P by aggregates. *Reactive mass* was defined as the fraction of the total soil mass given a depth of penetration of freshly added P into aggregates. It was measured by adding solution P into a mixture of aggregates containing low water content (Linquist et al., 1997). The total P in the differing aggregate fractions was measured after the mixture was separated into differing aggregate fractions. Further P penetration into aggregates with rapid movement of water into the aggregates containing low moisture content may, however, overestimate the depth of penetration of P into aggregates. On the other hand, attaching small aggregates onto large aggregates and breaking up large aggregates into small ones may increase P content in the large aggregates and decrease P content in the small ones when the mixture of differing aggregate fractions was dried and sieved.

In this experiment, *effective mass* was defined as the proportion of the total soil mass occupied by the added P in aggregates to estimate distribution of added P among aggregates. It was calculated as the soil mass in the "diffusion layer" divided by the total soil mass of the aggregate. It can be calculated using the following equation, assuming that aggregates approximate spheres of a uniform density:

$$\textit{Effective mass} = \frac{4/3\pi\,[(D/2)^3 - (D/2 - D_{eff})^3]\,\rho}{4/3\pi (D/2)^3\,\rho} = \frac{(D/2)^3 - (D/2 - D_{eff})^3}{(D/2)^3} \qquad (3.2)$$

where ρ is the soil aggregate bulk density, D is the aggregate diameter (mm), and D_{eff} is the depth of diffusion of P into aggregates. Effective mass (kg kg^{-1}) is defined to be one if the aggregate radius is less than or equal to D_{eff}.

The depth of diffusion of P (D_{eff}) in aggregates was estimated using the average linear diffusion distance (LDD). The linear diffusion distance, the distance an ion diffuses in time t with a diffusion coefficient of D_e, is $(2D_et)^{1/2}$ (Barber, 1980). The P diffusion coefficient of 1.5×10^{-12} $cm^2 s^{-1}$ reported by Nye and Stauton (1994) was used to estimate the depth of P diffusion assuming that the diffusion coefficient is independent of soil type and aggregate size. In a study on migration of P into aggregated particles of ferrihydrite, Willet et al. (1988) obtained a mean depth of 21 μm with the standard error 1.1 μm after 1 day reaction of P with ferrihydrite aggregates. The corresponding P diffusion coefficient would be 2.6×10^{-11} cm^2 s^{-1}, which is tenfold higher than the values reported by Nye and Stauton (1994). The larger D_e could be expected because of greater water contents used in their studies. In the study of Willet et al. (1988), P sorption was determined with a batch equilibrium. Thus water content was not a limiting factor influencing P diffusion into aggregates. In the study of Nye and Stauton (1994), an estimate of field water holding capacity was used in the incubation of soils with added P. The lower diffusion coefficient was expected because lower soil moisture content decreased P diffusion probably through influencing impedance (*f*). For the present experiment, the diffusion coefficient from Nye and Stauton (1994) was adopted because incubation studies mimicked field conditions.

The time intervals between the last fertilization and sampling were 72, 90, and 38 months for the Wahiawa, Kapaa, and Leilehua soils, respectively. The corresponding values of predicted depth of P diffusion into aggregates (LDD) were 0.238, 0.266, and 0.173 mm for the Wahiawa, Kapaa, and Leilehua soils.

The difference between "effective mass" as used in this study and "reactive mass" used by Linquist et al. (1997) is in the differing methods of estimating the depth of movement of added P into aggregates. Reactive mass estimates penetration of initially sorbed P into aggregates while effective mass estimates diffusion of sorbed P into aggregates assuming the initial P sorption occurred on the outer surfaces of aggregates. When a P fertilizer is applied to a soil, a complex sequence of reactions follows. Phosphate sorption occurs after dissolution of P fertilizer takes place and the P moves to an outer zone of fertilizer particles in which P concentration is lower (Barrow, 1980). Phosphorus sorption may be dependent on P diffusion from the fertilizer granule to aggregates upon mixing the soil. The initial rapid P sorption observed in the laboratory may not occur in exactly the same manner in field. The magnitude of decreasing extractable P with time in the incubation study is usually much greater than that due to the "P slow reaction", which is a slower diffusion controlled process following the initial adsorption reaction of P by Fe and Al (Barrow, 1985). The effective mass based on P diffusion is, therefore, speculated to better represent soils actually associated with sorption of P fertilizer.

The concentration of added P in "the diffusion layer", which is the depth of diffusion of sorbed P into aggregates, is assumed to be the same for aggregates regardless of size when P is added to a whole soil or to a mixture of differing aggregate fractions. This can be valid if 1) initial P sorption (perhaps within one second) per unit of surface area is the same for aggregates of varying size, and 2) the distribution of sorbed P occurs only through P diffusion into aggregates and among aggregates. Evidence for the first condition is provided by observations of Gunary et al. (1967), and Willet et al. (1988). Diffusion of P between aggregates is probably the result of diffusion of sorbed P in intra-aggregate pores.

Statistical Analysis

A split-plot design was used for analyzing the effects of aggregate size and P levels on 0.5 *M* $NaHCO_3$ extractable P, with main-plot treatments being P levels and blocks, and split-plot treatments being aggregate size. Pearson correlation coefficients were used as a measure of linear association between two measured variables. Simple and multiple regression were used to predict extractable P from selected soil properties such as the outer surface area of aggregates, aggregate size, and effective mass. For the multiple regression analysis, the AIC statistic was used to determine the best fitting model. The AIC statistic, the likelihood version of Cp statistic, provides a convenient criterion for selecting among candidate models (Statistical Science, 1995). Only the best fitting model, however, was reported with the estimated coefficients of variables and the coefficient of determination.

A ridge regression method was used to reduce multicollinearity among regressors when the regressors were highly correlated with one another. Choice of k for ridge regression was based on a C_p-like statistic (C_k). Procedurally, the use of the C_k statistic involved a simple plotting of C_k against k with the use of the k-value for which C_k is minimized (Myers, 1990). PRESS was also considered for choosing k values. The rationale for choosing k in this experiment was based on maximizing predicting ability (minimizing C_k) and on obtaining regression coefficients with sensible signs.

The standard deviation was used to characterize variation of a treatment while the standard error was used for comparing two treatments when necessary.

All statistical analysis was performed with S-PLUS version 3.3 (Statistical Science, 1995).

RESULTS AND DISCUSSION

Phosphorus Distributions among Aggregates

Changes in extractable P by 0.5 *M* $NaHCO_3$ with soil aggregate size varied with the soils studied. For the Kapaa and Leilehua soil samples with previously applied P (38 months and 7.5 years after P fertilization for the Leilehua and Kapaa soils, respectively), there were significant differences in extractable P for different aggregate sizes (Table 3.1 and 3.2). Extractable P in aggregates decreased with increased aggregate size in samples from field plots to which P had been applied (Figure 3.1 and 3.2). The increase in extractable P with decreased aggregate size became more significant with increased added P for the Kapaa soil (Figure 3.1), suggesting an interaction between P level and aggregate size. For control samples (0.003 mg P L^{-1}, and 0 P), there was little change in extractable P with aggregate size (Figure 3.1 and 3.2).

For the Wahiawa soil, 6.5 years after P fertilization, there was little change in extractable P with aggregate size (Table 3.3, Figure 3.3) except for extractable P at the highest P level (1.6 mg P L^{-1}). There was a statistically significant interaction between P level and aggregate size, which appears (Figure 3.3) to be due to slight effects of aggregate size occurring only at the highest P level (1.6 mg P L^{-1}).

Table 3.1. ANOVA table of the split-plot design for extractable P by 0.5 *M* $NaHCO_3$ in the Leilehua soil. Block effect was random, the others were fixed.

Source of variation	df	Sum of Sq	Mean of Sq	F value	*p*
P treat	1	1949.28	1949.28	2074.86	0.0005
Block	2	1.80	0.90	1.48	0.243
P treat x Block	2	1.88	0.94	1.55	0.228
Size	8	810.91	101.36	167.21	<0.0001
Size x P treat	8	792.00	99.00	163.31	<0.0001
Residuals	32	19.40	0.61		

Table 3.2. ANOVA table of the split-plot design for extractable P by 0.5 *M* $NaHCO_3$ in the Kapaa soil. Block effect was random, the others were fixed.

Source of variation	df	Sum of Sq	Mean of Sq	F value	*p*
P treat	3	889710.5	274730.1	50.08	0.103
Block	1	3509.1	69029.3	6701.87	<0.0001
P treat x Block	1	5485.8	5485.8	532.60	<0.0001
Size	8	14524.8	1815.6	176.27	<0.0001
Size x P treat	24	21685.2	903.6	87.73	<0.0001
Experimental error	16	164.5	10.3	0.77	0.713
Sampling error	72	968.1	13.4		

Table 3.3. ANOVA table of the split-plot design for extractable P by 0.5 *M* $NaHCO_3$ in the Wahiawa soil. Block effect was random, the others were fixed.

Source of variation	df	Sum of Sq	Mean of Sq	F value	*p*
P treat	3	1143780.0	381260.0	204.05	0.050
Block	1	51533.7	51533.7	5999.27	<0.0001
P treat x Block	1	1868.4	1968.4	229.15	<0.0001
Size	8	150.1	18.77	2.19	0.090
Size x P treat	24	480.5	20.02	2.33	0.040
Experimental error	16	137.4	8.59	1.18	0.300
Sampling error	72	526.6	7.31		

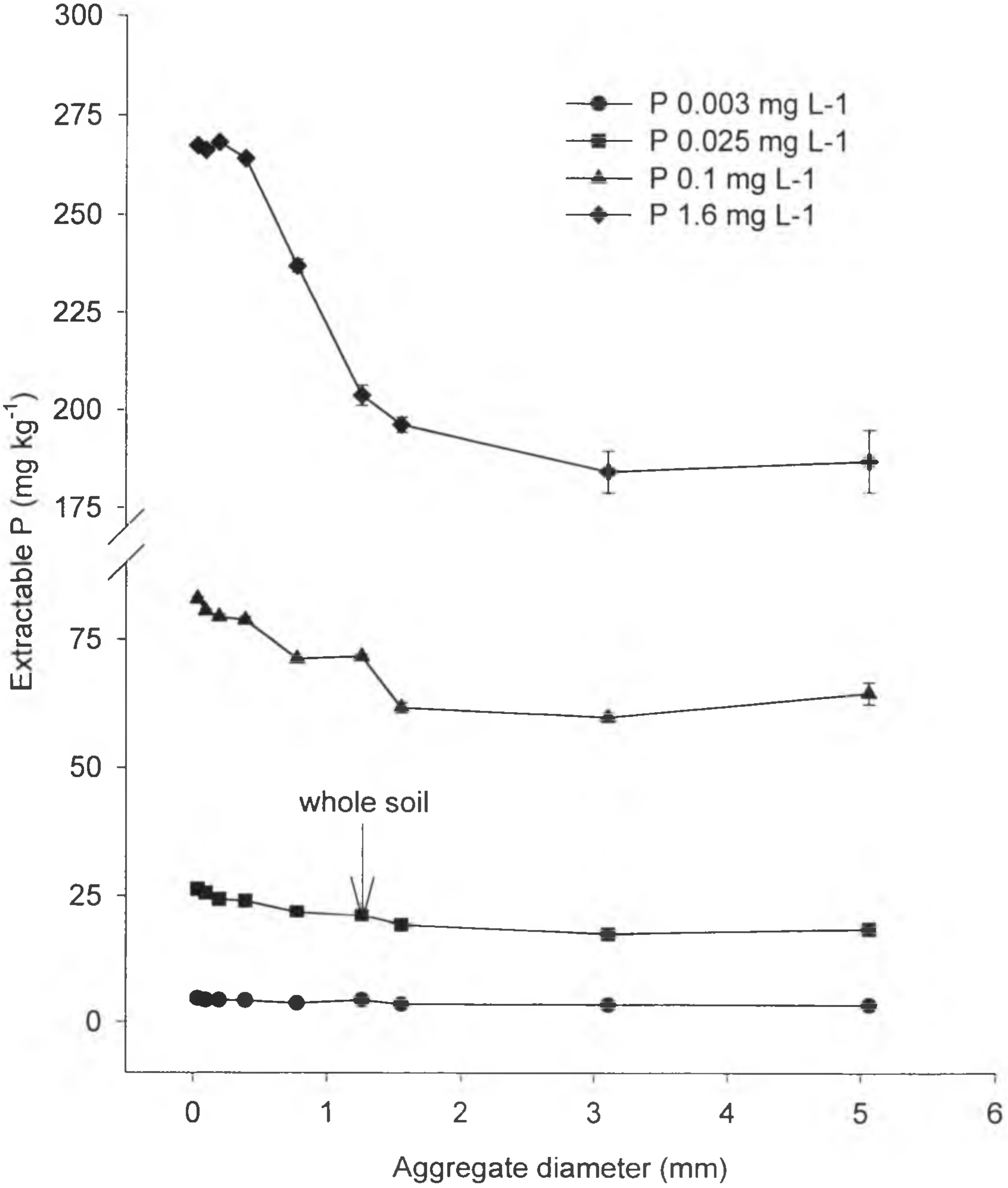

Figure 3.1. Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate size for the Kapaa soil. Error bars represent one standard deviation. Symbol sizes may exceed error bars in some cases. Phosphorus was applied in 1987.

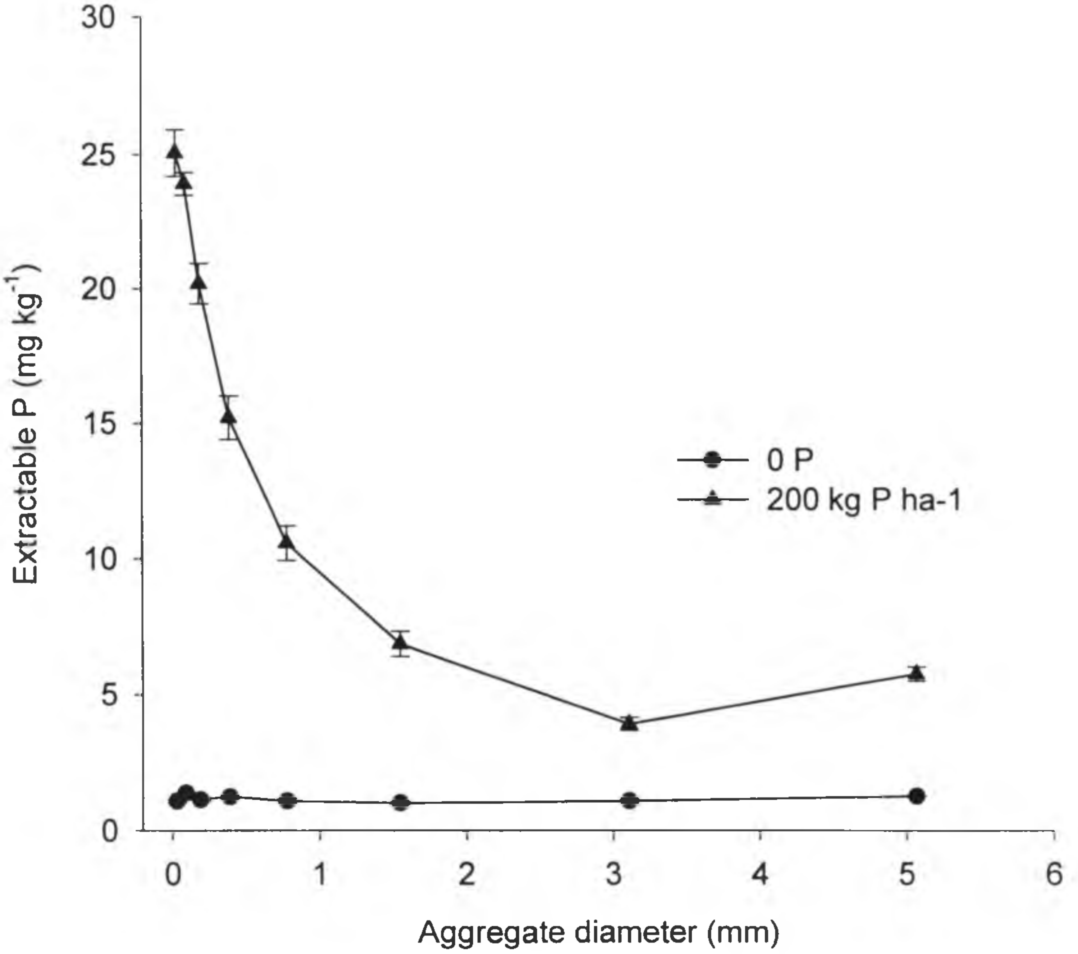

Figure 3.2. Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate diameter for the Leilehua soil. Error bars represent one standard deviation. Symbol size may exceed error bars in some cases. Phosphorus was applied in 1993.

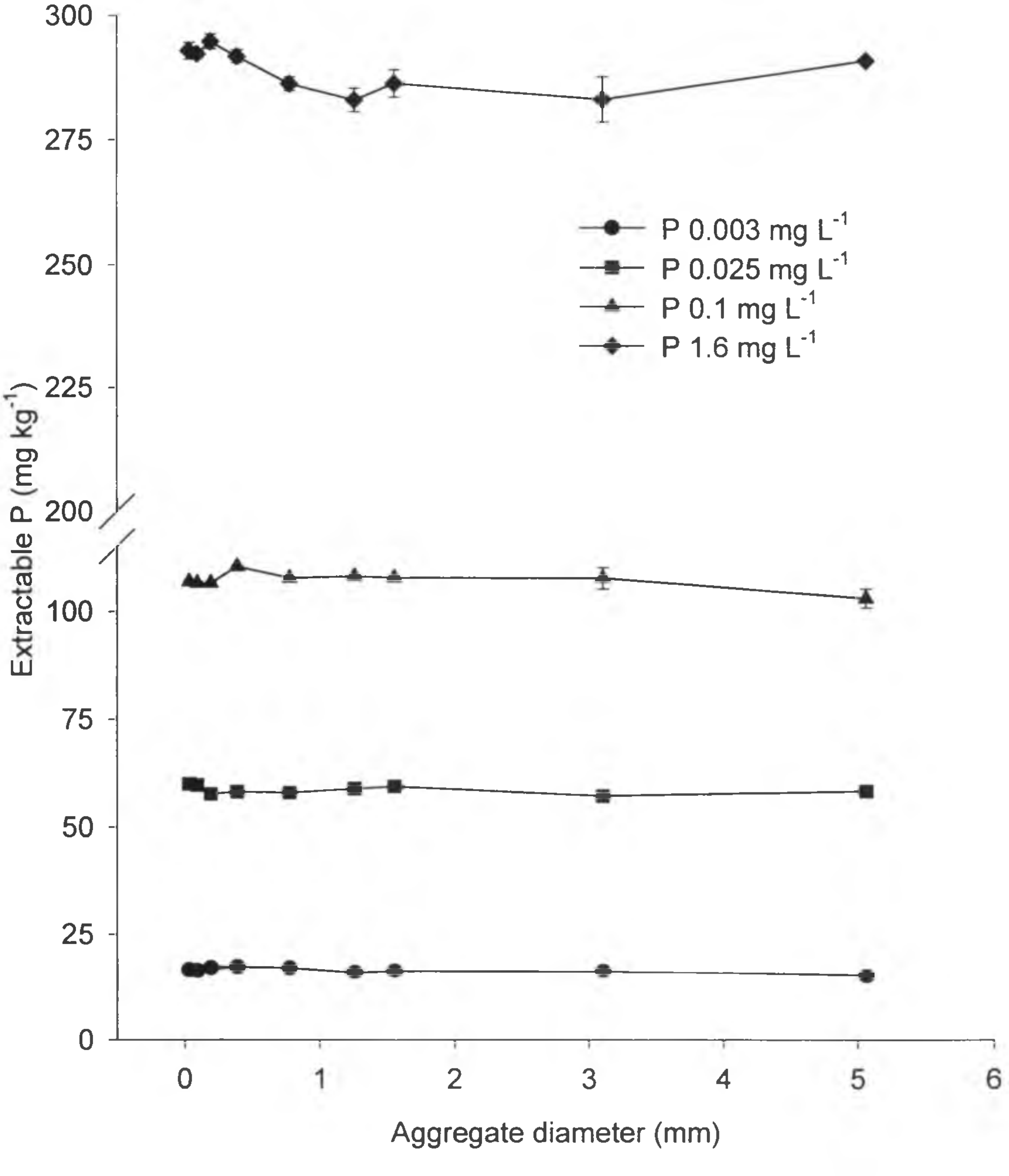

Figure 3.3. Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate diameter for the Wahiawa soil. Error bars represent one standard deviation. Symbol size may exceed error bars in some cases. Phosphorus was applied in 1989.

To further reveal the relationship between extractable P and aggregate size, inorganic and organic P extracted by 0.1 *M* NaOH was measured for the aggregates of the Leilehua soil. The results are shown in Table 3.4 and Figure 3.4. The changes in both inorganic and total P in the 0.1 *M* NaOH extractant with aggregate size were similar to those in the 0.5 *M* $NaHCO_3$ extractant where P had been applied while organic P among the aggregates were small for both no P and P applied samples .

The recovery of P with 0.1 *M* NaOH was 87 % of the added P for the Leilehua soil (Table 3.5), and was not significantly influenced by added P levels or aggregate size (Table 3.6). Willet et al. (1988) showed that P sorbed by ferrihydrite for 90 days was completely recovered by extraction with 0.1 *M* NaOH. These results indicated that the change in extractable P with aggregate size was primarily due to differential distribution of added P among aggregates. This change will diminish with the redistribution of added P due to P diffusion.

Contributions of P in Aggregates to Whole Soil

The mean (X_p) of extractable P in aggregates weighted by aggregate size distribution was calculated as follows:

$$X_p = \sum_{i}^{n} P_i w_i \qquad (3.3)$$

where P_i is the extractable P in aggregates, and w_i is the proportion of the total sample weight occurring in the corresponding size fraction. N is the number of size fractions.

Table 3.4. ANOVA table of the split-plot design for extractable P by 0.5 *M* NaOH in the Leilehua soil. Block effect was random, the others were fixed.

Source of variation	df	Total extractable P		Inorganic P		Organic P	
		Mean of Sq[†]	F value	Mean of Sq	F value	Mean of Sq	F value
P treat	1	3453982	717.46^{**}	3582423	8292.65^{**}	1172	0.16^{ns}
Block	2	6034	2.04^{ns}	462	0.13^{ns}	9098	2.70^{ns}
P treat x P treat	2	4814	1.63^{ns}	432	0.13^{ns}	7500	2.22^{ns}
Size	8	172004	59.26^{**}	203831	59.31**	2801	0.53^{ns}
Size x P treat	8	150328	50.92^{**}	195715	56.95^{**}	4253	1.26^{ns}
Residuals	32	2982		3437		3371	

[†] Mean of Squares.

** Significant at p≤ 0.01.

ns Not significant at p≤ 0.05.

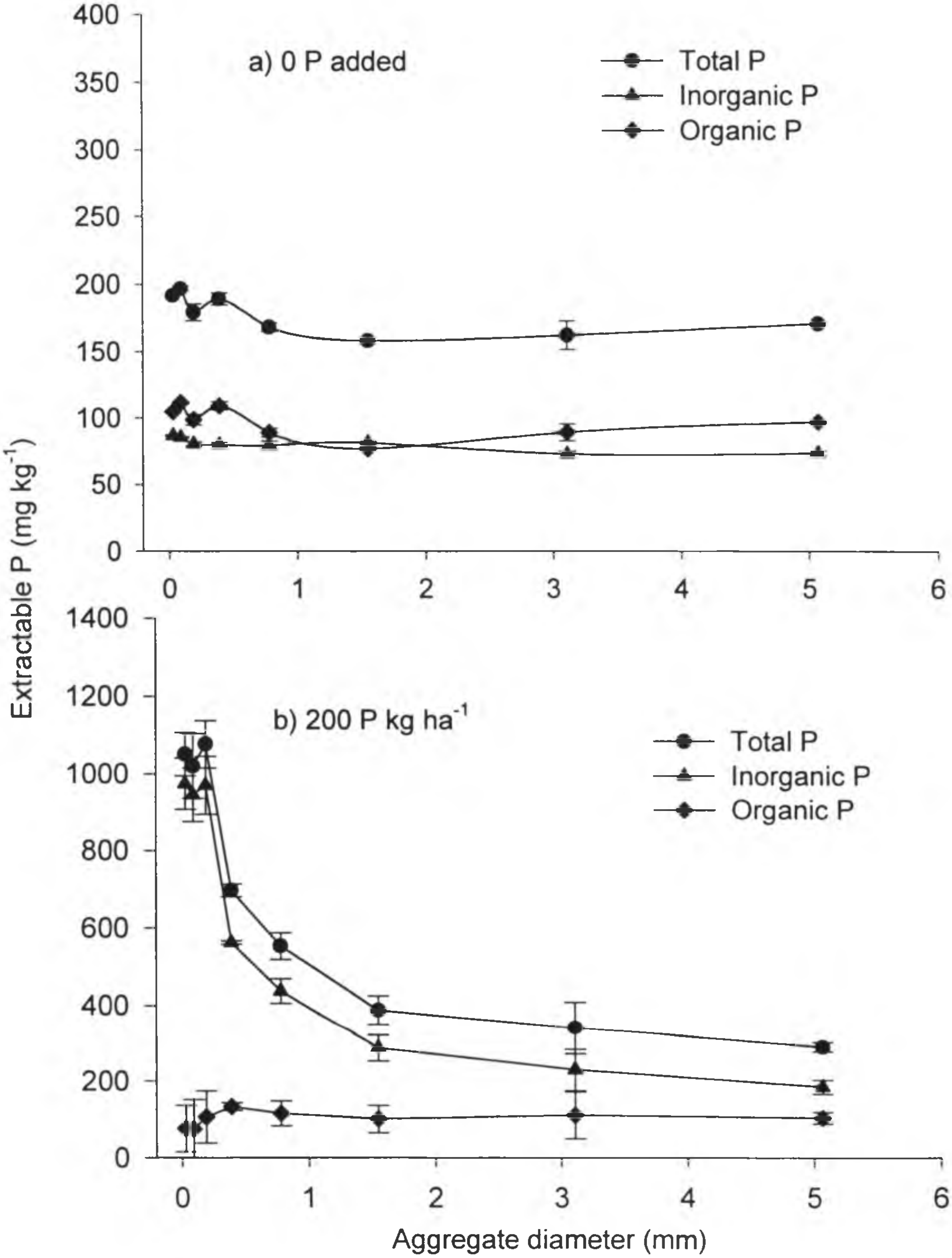

Figure 3.4. 0.1 *M* NaOH extractable P fractions among aggregates of the Leilehua soil. Error bars represent one standard deviation. Symbol size may exceed error bars in some cases. Phosphorus was applied in 1993.

Table 3.5. Effects of added P level and aggregate size on extractability of P by 0.1 *M* NaOH after 30 days reaction of P with the aggregates of the Leilehua soil.

P added	4-6 mm	2-4 mm	1-2 mm	Mean
mg P kg^{-1}		Extracted by NaOH (%)[†]		
200	90	87	82	86
400	93	85	80	86
800	88	90	83	87
Mean (%)	90	88	82	87

[†] Extractability (%) = (extractable P in P added sample - extractable P in no P added sample) / (total added P) x 100.

Table 3.6. ANOVA statistics comparing effects of applied P levels and aggregate diameter on extractability of P by 0.1 *M* NaOH for the Leilehua soil.

Factor	df	SS	MS	F value	*p*
P level (A)[†]	2	4.35	2.17	0.044	0.957
Diameter (B)[†]	2	167.72	83.86	1.701	0.210
A x B	4	82.36	20.59	0.418	0.794
Residuals	18	887.21	49.29		

[†] P level and Diameter were considered as fixed effects.

The weighted means of extractable P were very close to the measured extractable P in the whole soils (Table 3.7). The contribution of extractable P from each aggregate fraction to extractable P in the whole soil may, therefore, be expressed as a fraction of the weighted mean for each aggregate fraction, i.e.

$$Fraction\ (\%) = \frac{P_i w_i}{X_p} \qquad (3.4)$$

An aggregate size with a higher fraction indicates a greater contribution of extractable P from this aggregate fraction to the whole soil.

Table 3.7. Comparison of extractable P in the whole soil with weighted means from aggregates and aggregate size distribution for the three soils.

<table>
<tr><th rowspan="2" colspan="2">Soil</th><th colspan="4">P applied (mg P kg^{-1} soil)</th></tr>
<tr><th colspan="2">0</th><th colspan="2">200</th></tr>
<tr><td rowspan="2">Leilehua</td><td>Measured[†]</td><td colspan="2">1.04</td><td colspan="2">7.03</td></tr>
<tr><td>W.M[‡]</td><td colspan="2">1.12</td><td colspan="2">9.82</td></tr>
<tr><td colspan="2" rowspan="2"></td><td colspan="4">P applied (mg P L^{-1})[§]</td></tr>
<tr><td>0.003</td><td>0.025</td><td>0.100</td><td>1.600</td></tr>
<tr><td rowspan="2">Kapaa</td><td>Measured</td><td>4.3</td><td>21.1</td><td>71.6</td><td>203.7</td></tr>
<tr><td>W.M</td><td>3.5</td><td>19.1</td><td>64.2</td><td>200.4</td></tr>
<tr><td rowspan="2">Wahiawa</td><td>Measured</td><td>16.0</td><td>58.9</td><td>108.1</td><td>282.9</td></tr>
<tr><td>W.M</td><td>16.8</td><td>58.6</td><td>107.6</td><td>289.3</td></tr>
</table>

[†] Measurement of extractable P in the whole soil.

[‡] Weighted mean on the basis of extractable P in the aggregates and aggregate size distribution.

[§] Desired P concentration in soil solution for the field treatment estimated by the Fox and Kamprath method (1970).

The contributions of extractable P from differing aggregate fractions to the extractable P in the whole soil were, consequently, related to both extractable P in aggregates and the distribution of aggregate size. For P-added samples of the Leilehua soil, the contributions of extractable P from the larger aggregate fractions (2-6, 0.84-2, 0.42-0.84 mm) to the whole soil were relatively similar as the smallest aggregate (0-0.1

mm) (Figure 3.5). The contributions from the other groups of the aggregates were relatively small. For the 0 P treatment, the contribution of extractable P from each aggregate to the whole soil matched the pattern of aggregate size distribution due to similar extractable P contents among the aggregates.

For the Kapaa soil the contribution of extractable P from each aggregate fraction to extractable P in the whole soil increased with increased aggregate size although the decrease in levels of extractable P (Figure 3.6). This was due to the high proportion of large aggregates in this soil (Chapter 2).

Extractable P in soils was, therefore, related to extractable P in aggregates and to aggregate size distribution. Evaluating P availability should consider the effects of these factors on extractable P and plant root growth. Studies of nutrient uptake with aggregates of differing aggregate fractions showed that P uptake from small aggregates was greater than that from large aggregates (Wiersum, 1962; Cornforth, 1968; Misra et al., 1988a). Misra et al. (1988a) attributed this difference in P uptake to mechanical impedance to root penetration. Unfortunately, none of these papers reported the change in extractable P with aggregate size.

Factors Affecting P Distribution among Aggregates

Several factors may be responsible for the changes in extractable P with aggregate size. These factors may include soil physical, mineralogical, biological and chemical properties as well as preferential uptake of P from different aggregates by plant roots. The mineralogical composition and selected soil properties changed very little with

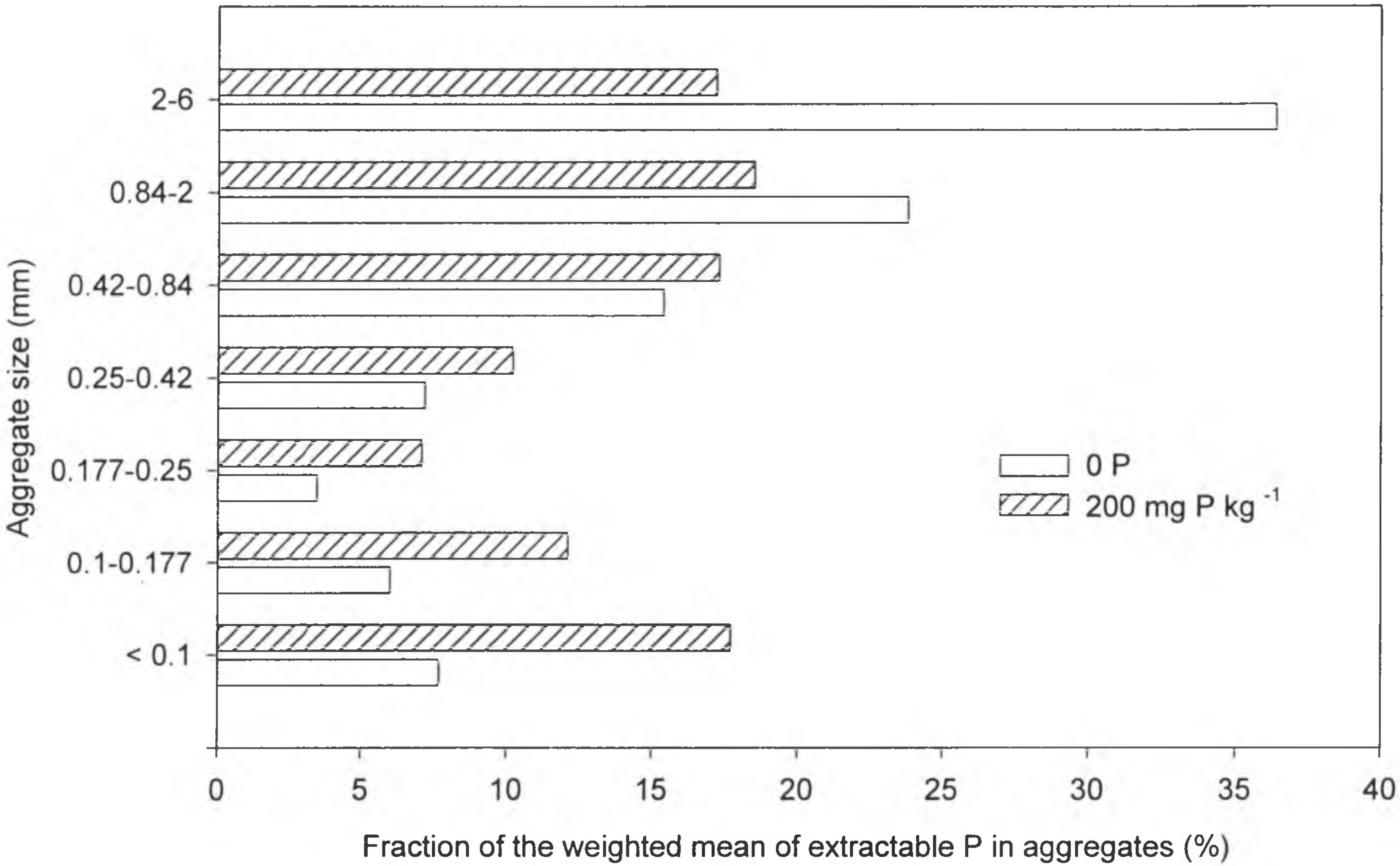

Figure 3.5. Contribution of 0.5 *M* $NaHCO_3$ extractable P from each aggregate fraction to extractable P in the whole soil for the Leilehua soil.

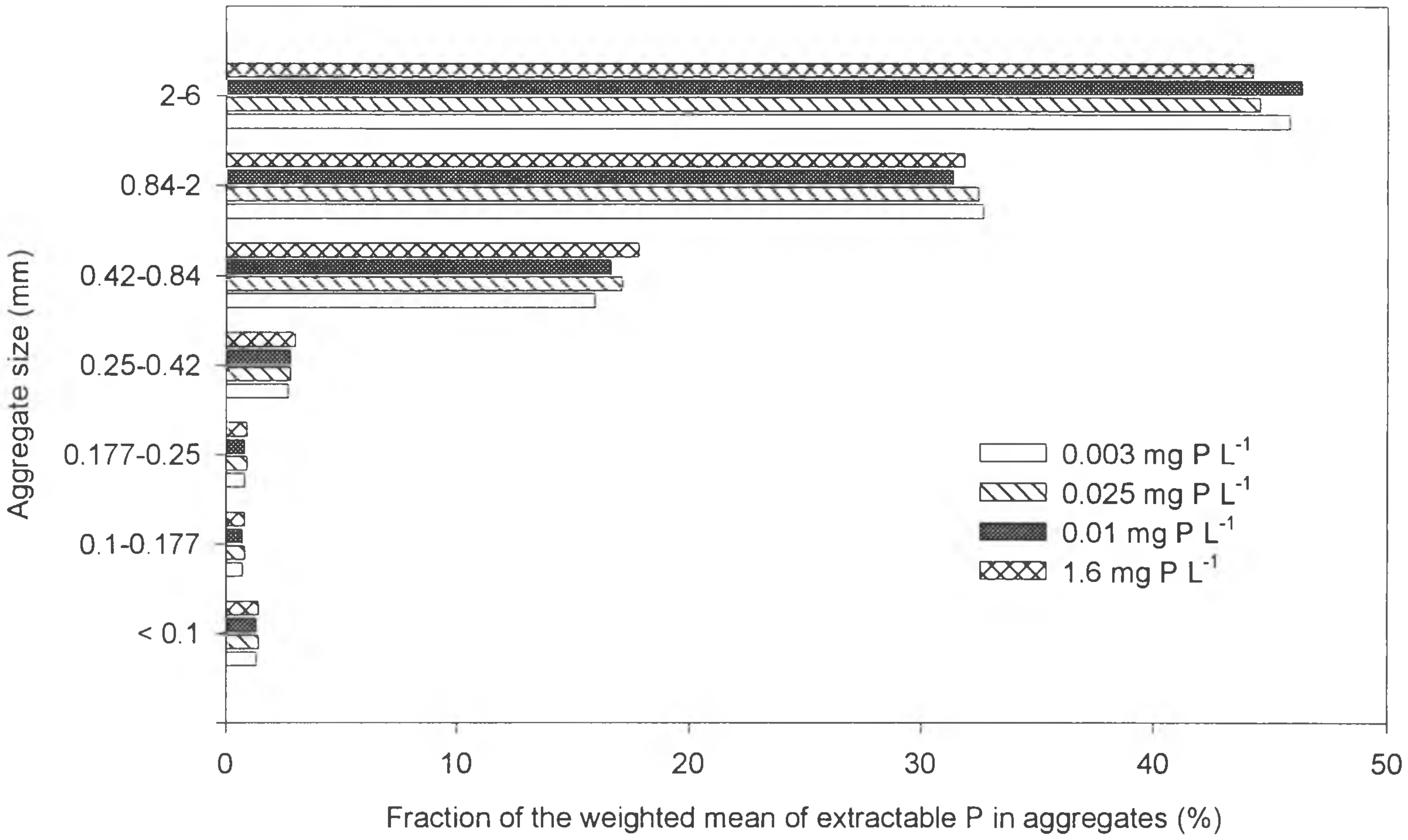

Figure 3.6. Contribution of 0.5 *M* $NaHCO_3$ extractable P from each aggregate fraction to extractable P in the whole soil for the Kapaa soil.

aggregate size (Chapter 2). The following discussion focuses on the effects of soil aggregation, mainly measures of aggregate size, on P sorption, diffusion, and extractable P in aggregate fractions.

1) Surface area of aggregate

Extractable P in aggregates is related to added P and original P in aggregates. Hence, the distribution of extractable P is dependent on the distribution of added P among aggregates if the level of original P in aggregates is similar.

Phosphorus sorption should be dependent on the aggregate surface area if other soil properties related to P sorption are relatively similar among aggregates of a soil. The initial rapid P sorption may be dependent on the outer surface area of aggregates due to the low mobility of P in the soils with high P retention. Gunary et al. (1967) showed that added P was initially sorbed on the periphery of synthetic aggregates. Using autoradiography of sorbed ^{32}P and P sorption studies, Linquist et al. (1997) found that added P was initially sorbed into a 0.188 mm layer around soil aggregates and apparently remained in this peripheral layer for at least 28 days. These results indicate that smaller aggregates with greater surface area per mass should sorb more P than larger aggregates.

The differences in P extracted with 0.5 *M* $NaHCO_3$ and with 0.1 *M* NaOH between P treatments and the no-P treatment were not significantly related to the outer surface area of aggregates for any of the three soils (data not shown). The increased extractable P associated with fertilization corresponded to an increasing outer surface area of aggregates in logarithmic scale for both the Kapaa and Leilehua soils (Figure 3.7-

8). There were highly significant correlations between the increase in extractable P and the natural logarithm of outer surface area (LogSA) at $p = 0.001$. The increase in extractable P, however, reached a maximum level at aggregate size 0.25-0.5 mm for the Kapaa soil (Figure 3.7). Extractable P in aggregates of diameter less than 0.25-0.5 mm did not further increase with increased log of outer surface area of aggregates, especially in the higher P treatment plot (1.6 mg P L^{-1}). For the Leilehua soil, the increase in 0.1 *M* NaOH extractable P reached a maximum level at aggregate size 0.125-0.25 mm (Figure 3.8a). Extractable P in aggregates of diameter less than 0.125-0.25 mm did not further increase with increased log of outer surface area. The increase in 0.5 *M* $NaHCO_3$ extractable P increased with log of surface area until an aggregate size of 0.053-0.125 mm (Figure 3.8b). There was a small difference in extractable P for aggregate fractions less than 0.125 mm.

There was little change in extractable P by 0.5 *M* $NaHCO_3$ with decreasing aggregate size for the Wahiawa soil (Figure 3.9).

Such relationships between extractable P and surface area suggest outer surface area is related to P sorption capacity (potential) rather than to the amount of sorbed P in aggregates. The distribution of added P among aggregates is probably influenced by diffusion of sorbed P into and among aggregates. From this viewpoint, effective mass may be used to estimate distribution of added P among aggregates by calculating the distance of diffusion of sorbed P into aggregates (see equation 3.2). Further relationships of P sorption and extractable P to the surface area and effective mass are discussed in the next section.

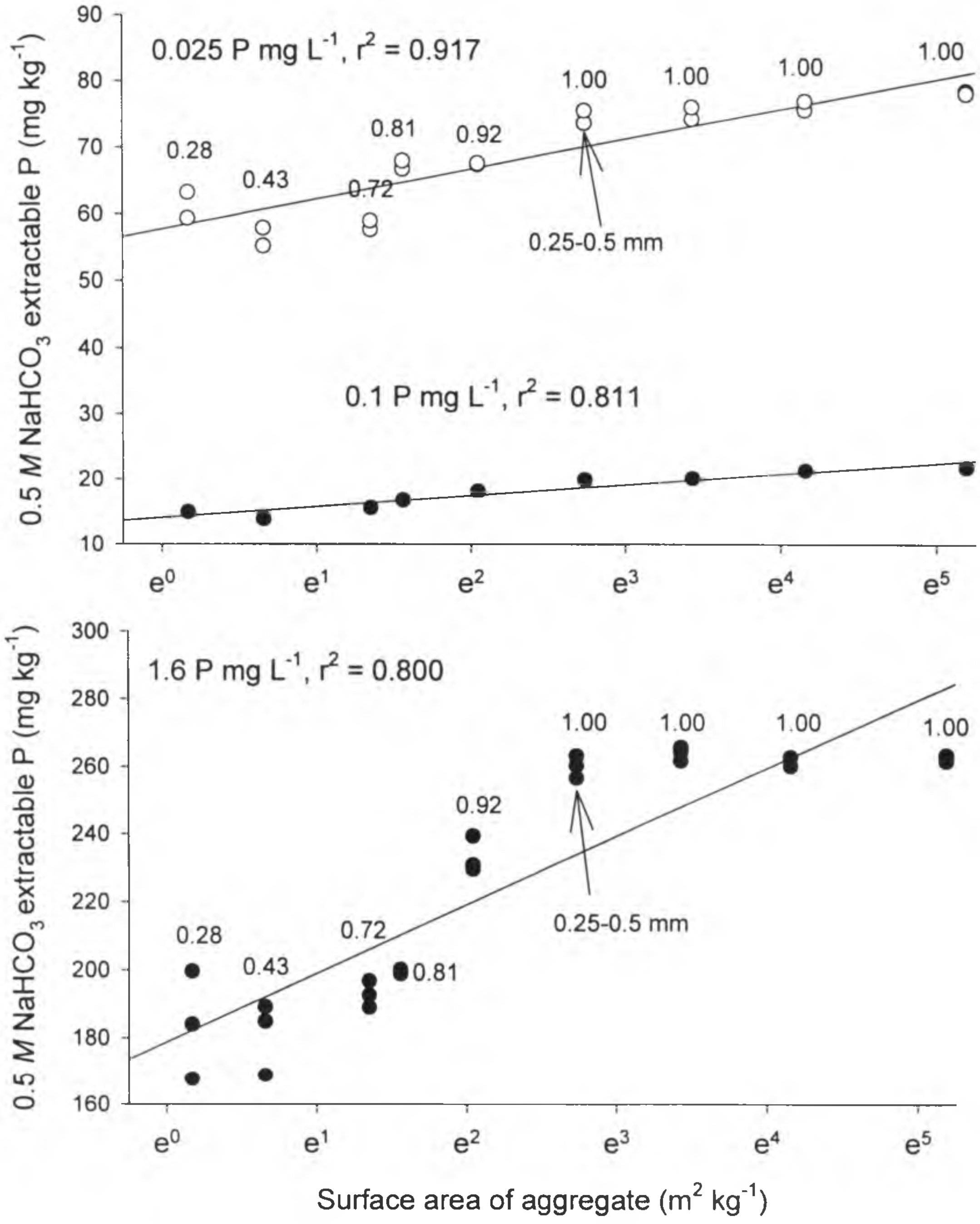

Figure 3.7. Relationship between the increase in 0.5 M NaHCO$_3$ extractable P and surface area of aggregates for the Kapaa soil. Numbers beside the points on the plots are effective mass.

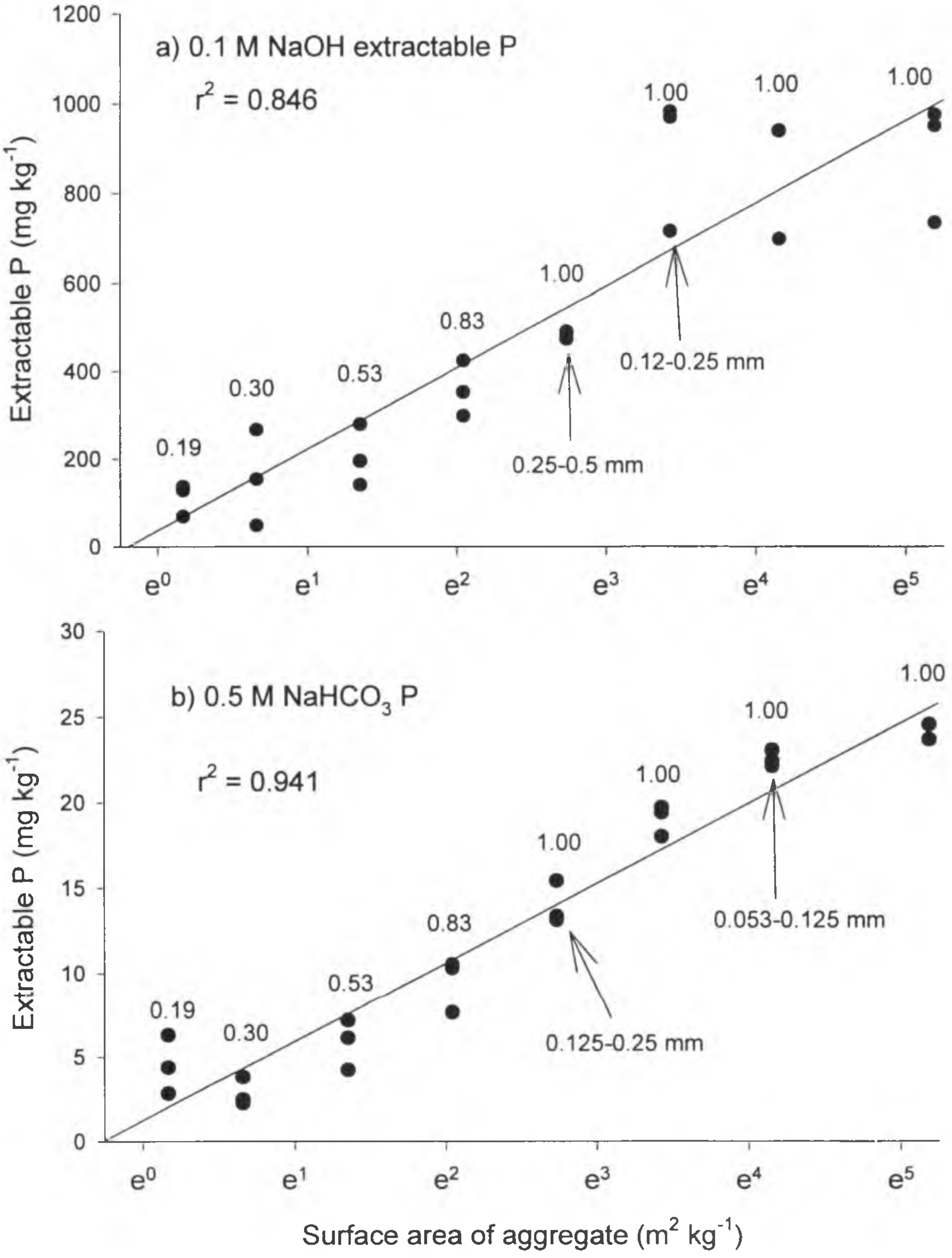

Figure 3.8. Relationship between the increase in extractable P and surface area of aggregates for the Leilehua soil. (a) extractable P by 0.1 M NaOH; (b) extractable P by 0.5 *M* NaHCO$_3$. Numbers beside the points on the plots are effective mass.

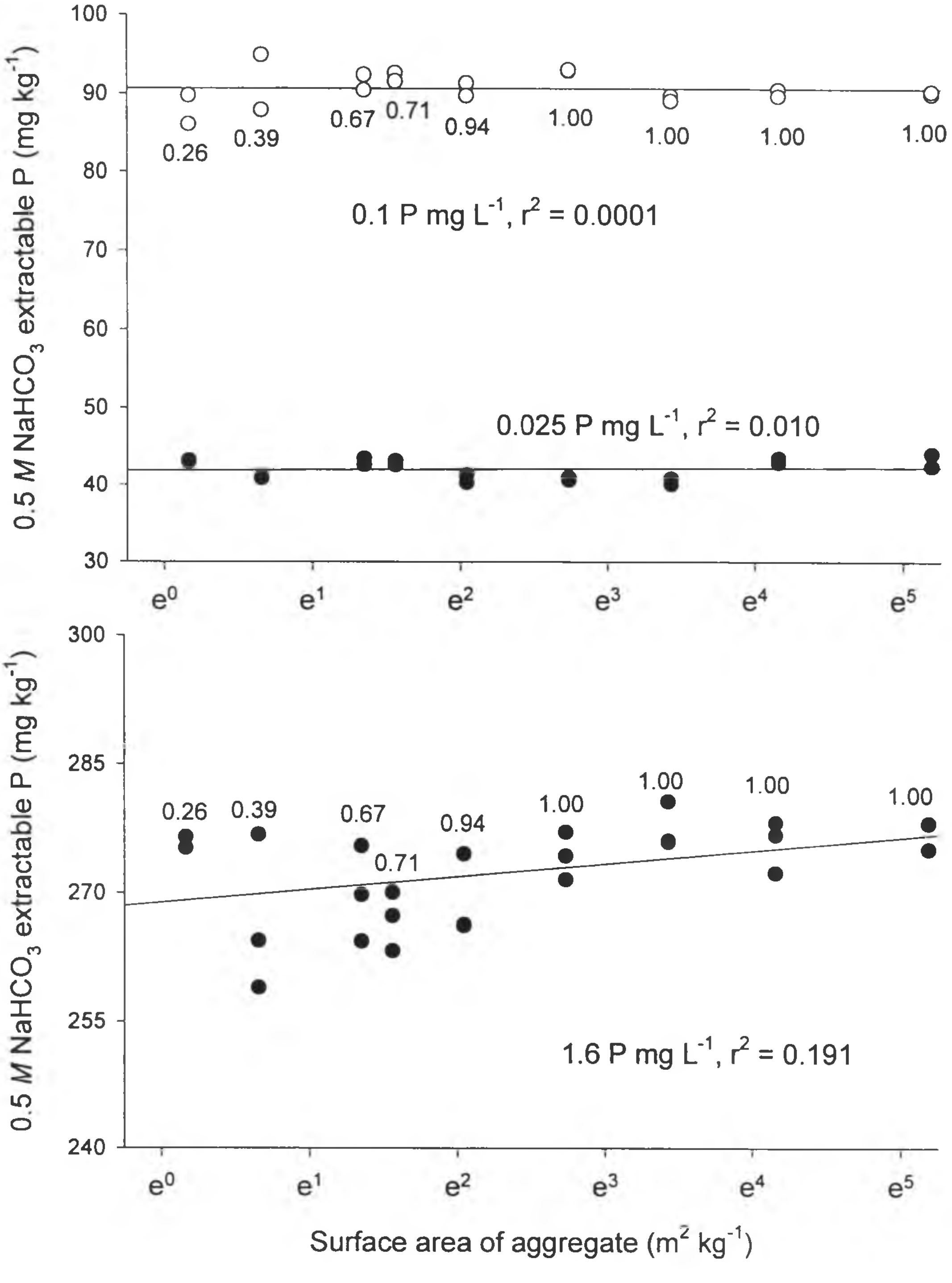

Figure 3.9. Relationship between the increase in extractable P with 0.5 M NaHCO$_3$ and surface area of aggregates for the Wahiawa soil. Numbers beside the points on the plots are effective mass.

The preferential P uptake from small aggregates by plant roots (Wiersum, 1962; Cornforth, 1968) may also decrease extractable P in small aggregates.

2) Effective Mass

Redistribution of initial sorbed P among aggregates due to P diffusion into and among aggregates should reduce the difference in extractable P among aggregates with time. Effective mass was used to estimate the distribution of sorbed P among aggregates. It is a proportion of the total soil mass predicted to be occupied by the added P. An aggregate with a larger value of effective mass should have more sorbed P per unit mass, and thus more extractable P.

The values of effective mass are shown in Table 3.8. For the Kapaa soil, the value of LDD was estimated at 0.266 mm for a time period of 7.5 years (time interval between the last fertilization and sampling). Effective mass increased from 0.28 to 1 as aggregate size decreased from 4-6 mm to 0.25-0.5 mm. Values of effective mass were the same for aggregates less than 0.25-0.5 mm. Extractable P by 0.5 *M* $NaHCO_3$ increased with increased effective mass (Figure 3.7). When the values of effective mass increased to 1 for aggregate fractions less 0.25-0.5 mm, the change in extractable P among these aggregates was small (Figure 3.7).

For the Leilehua soil, the average linear diffusion distance (LDD) was estimated at 0.173 mm for a time period of 38 months. The corresponding values of effective mass increased from 0.19 to 1 as aggregate size decreased from 4-6 mm to 0.25-0.5 mm (Table 3.8). Effective mass values were the same for aggregates less than 0.25-0.5 mm. The change in extractable P by 0.1 *M* NaOH with aggregate size corresponded to the change in effective mass (Figure 3.8a). 0.5 *M* $NaHCO_3$ extractable P from 4-6 mm to 0.25-0.5 mm increased with increased effective mass. 0.5 *M* $NaHCO_3$ Extractable P, however, continued to increase with decreasing aggregate size less than 0.25-0.5 mm (Figure 3.8b) even though effective mas was already 1 and there did not increase further.

Table 3.8. Effective mass, and volume weighted mean diameter (VWMD)† of each aggregate fraction for the Leilehua, Kapaa, and Wahiawa soils.

Size (mm)	VWMD (mm)†	Effective mass (kg kg^{-1})		
		Leilehua	Kapaa	Wahiawa
4 - 6	5.066	0.19	0.28	0.26
2 - 4	3.107	0.30	0.43	0.39
1 - 2	1.554	0.53	0.72	0.67
0.5 - 1	0.777	0.83	0.97	0.94
0.25 - 0.5	0.388	1.00	1.00	1.00
0.125 - 0.25	0.194	1.00	1.00	1.00
0.053 - 0.125	0.094	1.00	1.00	1.00
< 0.053	0.033	1.00	1.00	1.00
Whole soil (< 6)	‡	0.69	0.63	1.00

† The mean diameter of aggregates was calculated on a volume weighted basis using equation 3.1.

‡ The geometric mean diameter (GMD) of water stable aggregate was used to estimate effective mass. The values of GMD were 0.407, 1.062, and 1.876 mm for the Wahiawa, Leilehua, and Kapaa soils, respectively.

There was, however, a relatively uniform distribution of extractable P among aggregates for the Wahiawa soil (Figure 3.9) probably related to the low degree of aggregation in this soil. The values of GMD, estimated LDD, and estimated effective mass were 0.407 mm, 0.238, and 1.00, respectively. The value of estimated effective mass for the whole soil suggests that P on the surface of aggregates may diffuse into the center of the aggregate. The disparity between the uniform distribution of P among large-size aggregates (from 0.5-1 to 4-6 mm) and data shown in Table 3.8 was probably related to methods used for obtaining aggregates and soil pore size distribution. Larger aggregates obtained by a dry-sieving method may include a portion of small water stable aggregates, which contain greater extractable P which thus increases extractable P in the large aggregates. This may mask the differences in extractable P among aggregates.

The pore size distribution may also affect P distribution among aggregates. The fraction of pore volume with radii less than 66 µm (geometric mean of pore size) at 0.0045 MPa in the Wahiawa soil was greater than that in the Kapaa soil (Chapter 2). A higher proportion of pore size with radii between 30 and 66 µm (inter-aggregate pores) may decrease the soil tortuosity factor by reducing the path of P diffusion at a high soil moisture level, and thus increase P diffusion. Phosphorus diffusion should also be greater because of higher P concentrations found in leachates (see chapter 5). Thus, P mobility in the Wahiawa soil may be higher than in the Kapaa soil.

Predicting Extractable P with Surface area, Effective mass and Aggregate Size

Based on the discussion above, the outer surface area probably relates to P sorption capacity in aggregates while the effective mass is a proportion of the total soil mass predicted to be occupied by added P, through estimating the distance of diffusion of added P into aggregates. The P extraction from aggregates may also be influenced by aggregate size because the accessibility of an extractant to P in aggregates varies with aggregate sizes and stability. It was hypothesized that extractable P should be positively related to effective mass (EffMass), inversely related to outer surface area (InvSA), and negatively to aggregate size after P is applied to a whole soil or a mixture of aggregate fractions and the subsequently separated aggregate fractions are extracted. The natural logarithm of aggregate size (LogDiam) was used because water-stable aggregate size distribution was log-normal (Chapter 2). The use of InvSA was based on the assumption of the decrease in extractable P with increased P sorption capacity.

Pearson correlation coefficients between InvSA, EffMass, and LogDiam are shown in Table 3.9. These variables were highly correlated, and particularly aggregate diameter and effective mass. A ridge regression procedure, therefore, was used to reduce multicollinearity among these predictors (Myers, 1990). Multiple regression results, including ordinary least squares (OLS), are shown in Table 3.10. Generally speaking, ridge regression did not greatly change the values or signs of coefficients of regressors in most cases except for extractable P with 0.1 *M* NaOH on the Leilehua soil. The following discussion will, therefore, focus on the OLS results.

For the Leilehua and Kapaa soils, ninety percent or more of the variation in 0.5 *M* $NaHCO_3$ extractable P was accounted for by surface area, effective mass, and aggregate size (Table 3.10). The t-test showed that all estimated coefficients were highly significant (data not shown, OLS). For the Wahiawa soil, the variation in extractable P explained by these variables was small (20-30%) except for the 1.600 mg P L^{-1} treatment

(Table 3.10). Possible reasons that the model failed to predict extractable P from these variables were discussed in the previous section.

Table 3.9. Pearson correlation coefficients of independent variables for the three soils.

	Leilehua Soil		Kapaa Soil		Wahiawa Soil	
	LogDiam[†]	EffMass	LogDiam	EffMass	LogDiam	EffMass
EffMass[†]	-0.8929		-0.8265		-0.8474	
InvSA[†]	0.8520	-0.9543	0.8332	-0.9791	0.8322	-0.9733

[*] LogDiam: logarithmic transformation of aggregate size;
EffMass: effective mass;
InvSA: inverse of surface area.

The variation of extractable P with 0.1 *M* NaOH was mainly accounted for by LogDiam ($r^2 = 0.846$). The addition of surface area and effective mass to the regression equation did not substantially increase prediction of the extractable P (Table 3.10). The t-tests showed that coefficients for inverse of surface area (InvSA) and EffMass were not significantly different from zero at $p < 0.2$ (data not shown). However, effective mass accounted for 70% of the variation of extractable P for simple regression ($r^2 = 0.705$).

In simple regression analyses, considering only one independent variable at a time, extractable P was negatively related to aggregate diameter, and positively related to surface area and effective mass (both of which are negatively correlated with aggregate size). In the multiple regression, however, the coefficient for inverse surface area was positive, indicating a negative marginal relationship of extractable P to surface area once the relationships with two other independent variables are accounted for. The effect of

Table 3.10. Relationships of extractable P to aggregate size, surface area, and effective mass.

Extractant	P[†]	Reg[‡]	Intercept	LogDiam[§]	InvSA[§]	EffMass[§]	R^2
Leilehua Soil							
$NaHCO_3$	200	OLS	-3.235	-4.602	14.83	12.89	0.965
		Ridge	-2.312	-4.554	13.64	12.05	0.965
NaOH	200	OLS	-25.89	-168.5	397.0	427.6	0.858
		Ridge	103.0	-154.4	208.8	324.8	0.854
Kapaa Soil							
$NaHCO_3$	0.025	OLS	4.037	-1.433	11.24	13.24	0.984
		Ridge	4.274	-1.431	10.87	13.01	0.984
$NaHCO_3$	0.100	OLS	17.40	-4.037	43.10	48.28	0.915
		Ridge	21.55	-3.999	39.06	44.30	0.914
$NaHCO_3$	1.600	OLS	26.68	-14.30	147.7	196.7	0.903
		Ridge	42.29	-14.18	132.6	181.5	0.902
Wahiawa Soil							
$NaHCO_3$	0.025	OLS	46.14	-0.7153	-1.152	-5.446	0.261
		Ridge	44.36	-0.6210	0.2850	-3.518	0.251
$NaHCO_3$	0.100	OLS	98.98	0.8678	-12.61	-6.340	0.305
		Ridge	94.51	0.8020	-7.858	-2.056	0.283
$NaHCO_3$	1.600	OLS	240.8	-2.795	37.35	27.36	0.410
		Ridge	248.3	-2.766	29.78	20.09	0.402

[†] Units of applied P is mg P ha^{-1} for the Leilehua soils, and mg P L^{-1} (desired P concentration in soil solution based on the method of Fox and Kamprath (1970)) for the Kapaa and Wahiawa soils.

[‡] OLS and Ridge indicated ordinary least squares and ridge regressions, respectively.

[§] LogDiam: log of aggregate diameter; InvSA: an inverse of outer surface are; EffMass: effective mass.

aggregate size on the extraction process may be separated from the effect on P sorption because increased aggregate size would increase extractable P by reducing P sorption. The signs of the coefficient of aggregate size may not be the same for all experiments. When P was added to the whole soil and competition among aggregates occurred, the effect of aggregate size on extractable P in subsequently separated aggregates may reflect the effect of accessibility of solution to P in aggregates during the extraction process. When P was added to separated aggregates or to soils, extractable P may increase because less of the added P was sorbed by larger aggregates. Values of the P buffer coefficient were positively related to aggregate size (Wang et al., 1996).

The variation in extractable P among differing aggregate fractions in structured soils suggests that the sorption reaction of added P with aggregates is a slow process, and is probably limited by diffusion of sorbed P into aggregates. Phosphorus sorption at the sorbent-liquid interface is assumed to be instantaneous; the rate at which P is transported to this interface probably controls the attainment of equilibrium. These P reactions may, therefore, be still rapid once aggregates are broken up, or/and P is transported to the unoccupied sorption sites within aggregates. This will be discussed in Chapter 4.

CONCLUSIONS

Phosphorus extracted by 0.5 *M* $NaHCO_3$ and by 0.1 *M* NaOH increased with increased aggregate size where P had been applied to the Kapaa and Leilehua soils. Extractable P changed very little with decreasing aggregate size in control samples (no P applied). There was little difference in organic P among differing aggregate fractions for the Leilehua soil. The change in extractable P with aggregate size was largely associated with fertilization.

The decrease in outer surface area with increased aggregate size alone did not explain the decrease in extractable P with increased aggregate size, probably because P migrates into the aggregates. *Effective mass* was defined to estimate the distribution of added P among aggregates. The change in extractable P was successfully predicted from surface area, effective mass, and aggregate diameter for the Kapaa and Leilehua soils. There was, however, little change in extractable P with aggregate size in the Wahiawa soil. This may be related to the low aggregate stability of the Wahiawa soil compared to the Kapaa and Leilehua soils.

Extractable P in the whole soil was close to the mean of extractable P in aggregates weighted by corresponding aggregate size distribution. The contribution of extractable P from an aggregate fraction to the whole soil was dependent on extractable P in aggregates and aggregate size distribution.

CHAPTER 4

MECHANISMS HOW AGGREGATE SIZE AFFECTS THE DISTRIBUTION OF ADDED PHOSPHORUS AMONG AGGREGATES

ABSTRACT

Mechanisms how aggregate size affects the distribution of added P among aggregates has not been quantified although extractable P increased with decreasing aggregate size. The distribution of added P among aggregates affect soil P availability and may improve predicting P requirements in crop production systems. The effects of aggregate size on P status in the Leilehua soil from Hawaii were assessed with respect to P sorption, 0.5 *M* $NaHCO_3$ extractable P (available P), and 0.001 *M* $CaCl_2$ extractable (P in soil solution). After P was added to a mixture of differing aggregate size fractions, P sorption and extractable P in subsequently separated aggregates decreased as aggregate size increased from < 0.5 to 4 - 6 mm. The decline in available P with time was much greater than the decline in solution P. Continuous P reaction with unoccupied P sorption sites in soils is, therefore, hypothesized to explain the decline in fertilizer effectiveness with time. This hypothesis is further supported by evidence that the heterogeneity of available P among aggregates for highly aggregated soils remained even after 7.5 years.

By contrast, P sorption decreased, 0.001 *M* $CaCl_2$ extractable P increased as aggregate size increased after P was added to separated aggregate fractions. The change in 0.5 *M* $NaHCO_3$ extractable P with aggregate size was dependent on the level of P

added. At 0-200 mg P kg^{-1}, extractable P increased with increased aggregate size while extractable P was greater at both small and large aggregate sizes when 200 - 800 mg P kg^{-1} was added.

The results suggest that an increase in soil aggregation reduces P sorption, and increases extractable P. Thus grinding and shaking soil sample used in P analysis may over-estimated P requirements by under-estimating soil P availability because diffusion-limited P sorption sites are exposed to increase P sorption.

INTRODUCTION

Tropical soils with low surface-charge density and low clay activity usually have high aggregation (Uehara and Gillman, 1981). Studies of nutrient uptake with aggregates of varying size (Misra et al., 1988a) found that P uptake from small size aggregates was greater than that from large size aggregates. They attributed these results to the low mobility of phosphorus in soils and the decreasing accessibility of phosphorus within large aggregates by roots. Phosphorus diffusion within aggregates is very slow. Intra-aggregate P diffusion coefficient has been estimated from 1.5×10^{-12} cm^2 s^{-1} (Nye and Staunton, 1994) to 10^{-14} cm^2 s^{-1} (Vaidyanathan and Talibudeen, 1968).

Many studies have emphasized on the influence of structure on root development and ion movement. The direct influence of soil aggregation on the measurements of nutrient status in soils has, however, not been examined. Studies of the effect of aggregate size on phosphorus supply should include the influences of aggregate size on P sorption, desorption, and its availability to plants.

The inter- and intra-aggregate pore system affects both the accessibility of exchange sites (Brusseau and Rao, 1990; Horn et al., 1994), and desorption (Horn and Taubner, 1989) because the accessibility of solid to solution is reduced by soil aggregation. Phosphorus sorption decreased with increasing aggregate size (Linquist et al., 1997). The ratio of directly accessible reaction sites on the sample outer surface area to the sample mass will decrease with increasing aggregate diameter, assuming a spherical aggregate shape.

The P buffering coefficient (PBC) is the ratio of extractable P to added P, and an important parameter in making fertilizer P recommendations. Several soil properties have been used to predict PBC. Since soil aggregation reduces the accessible reaction sites, aggregate size may also influence PBC. The overall goal of this study is, therefore, to attempt to predict PBC and residual P from improved knowledge of the effect of soil aggregation on P dynamics.

MATERIALS AND METHODS

Soil

The soil used in this experiment was the Leilehua soil and its preparation was the same as described in Chapter 2 and 3. For the P sorption study, the air-dried soil (< 6 mm) was sieved into eight aggregate sizes with sieve openings 4, 2, 1, 0.5, 0.25, 0.125, and 0.053 mm. The corresponding aggregate sizes were 4 - 6, 2 - 4, 1-2, 0.5-1, 0.25-0.5, 0.125-0.25, 0.053-0.125, and 0-0.053 mm, with corresponding volume-weighted mean diameters of 5.066, 3.107, 1.554, 0.777, 0.388, 0.194, 0.094, and 0.033 mm. For the P incubation study, the air-dried soil was sieved into five aggregate sizes, 4-6, 2-4, 1-2, 0.5-1, and 0-0.5 mm. The corresponding volume-weighted mean diameters were 5.066, 3.107, 1.554, 0.777, and 0.315 mm.

Phosphorus Incubation Study

Experiment I (P Added to a Mixture of aggregates)

A mixture of equal amounts (100 g) of varying-size aggregates (0-0.5, 0.5-1, 1-2, 2-4, 4-6 mm) and the whole soil as a control were treated with P levels of 0, 57.41, 110.15, 224.63, 473.33, and 864.95 mg P kg^{-1} soil. Each P treatment was replicated ten times (in 10 plastic bags). To reduce the aggregate destruction, aggregates were slowly moisturized with P-free 0.001 *M* $CaCl_2$ solution using a sprayer before adding P solution to the container. A 0.001 *M* $CaCl_2$ solution containing P as $Ca(H_2PO_4)_2{\cdot}2H_2O$ was directly added to bring the soil to field capacity. The soil samples in plastic bags were exposed, and were allowed to go through wetting and drying cycles for 360 days. The soil samples were rewetted with deionized water when the sample had dried.

Incubated soil samples were sampled at the end of 14, 28, 60, 180, and 360 days. At each incubation period, two bags were used. The mixture was air-dried and separated into the original size fractions by the dry-sieving method. Duplicate samples for each aggregate fraction were analyzed for extractable P by 0.001 *M* $CaCl_2$ and by 0.5 *M* $NaHCO_3$ (Watanabe and Olsen, 1965). Extractable P by 0.001 *M* $CaCl_2$ and by 0.5 *M* $NaHCO_3$ were used to estimate the available P and solution P in aggregates. Total P in each aggregate fraction was measured after 28 days of incubation. Phosphorus sorption in aggregates was estimated from the difference between the total P in P-added aggregates and the total P in aggregates with 0 P added.

Experiment II (P added to Separated Aggregate Fractions)

In the second incubation study, P levels of 0, 57.41, 110.15, 224.63, 473.33, and 864.95 mg P kg^{-1} soil were added to separated aggregate fractions (250 g for each aggregate fraction). The aggregate fractions were <0.5, 0.5-1, 1-2, 2-4, and 4-6 mm, which had contained the same initial extractable P, and incubated for 28 days. The P treatments were replicated three times. At the end of incubation P was extracted by 0.001 *M* $CaCl_2$ (an estimate of solution P) and by 0.5 *M* $NaHCO_3$ (an estimate of available P). Phosphorus sorption was estimated from the P disappearance from the solution.

There is an important difference between these two incubation studies. Phosphorus was added to the mixture and then aggregates were separated after incubation in the first study, and in the second the aggregates were separated and then P was added to each fraction separately. Phosphorus in solution is distributed among differing aggregate fractions after P was added to the mixture (*Experiment I*), but P sorbed by each fraction is different due to different surface areas of differing aggregates. On the other hand, there is no competition for P sorption among aggregate fractions when P was directly added to each fraction (*Experiment II*). The difference in P sorption was reflected in P concentrations in solution when P was added to separated aggregate fractions.

The continuous reaction between P in solution and aggregates was also determined. Solution P in separated aggregate fractions (1-2, 2-4, and 4-6 mm) from the *Incubation Experiment II* for P levels of 473.33 and 864.95 mg P kg^{-1} was measured using three methods: (1) 0.001 M $CaCl_2$ extractable P with shaking aggregates for 15 minutes; (2) equilibrate aggregates with 0.001 M $CaCl_2$ without shaking for 36 hours; and (3) equilibrate aggregates with 0.001 M $CaCl_2$ without shaking for 8 days. The ratio of solution to soil was 20 to 1 for these three methods.

Phosphorus Buffering Coefficient

The P buffering coefficient (PBC) is defined as the increase in extractable P resulting from the addition of fertilizer P to the soil and is often used to calculate how much P to be added to the soil to meet plant P requirements. The phosphorus buffering coefficient was estimated by fitting a linear equation to extractable P data after adding P to separated aggregate fractions (*Experiment II*). Then, the relationship between PBC and aggregate size was modeled.

The 0.5 *M* $NaHCO_3$ extractable P in subsequently separated aggregate fractions was predicted using both PBC and sorbed P in aggregates after P was added to the mixture of differing aggregate fractions (*Experiment I*). A linear relationship between extractable P and added P was assumed.

Phosphorus Sorption Experiment

Two grams of each aggregate fraction and the whole soil (< 2 mm) were equilibrated in 50-ml containers (flat bottom) with 20 ml of a 0.001 *M* $CaCl_2$ solution containing 0, 11.00, 27.51, 56.68, 105.86, 168.61, 222.96, 269.97, and 545.77 mg P L^{-1} ($Ca(H_2PO_4)_2 \cdot 2H_2O$). The experiment was replicated two times. To reduce the aggregate destruction, aggregates were slowly moisturized with P-free 0.001 *M* $CaCl_2$ solution using a sprayer before adding P solution to the container. Samples were equilibrated with P solution for 1 and 6 days, respectively, at 298° K and swirled gently for 30 minutes every 30 minutes for the first day of incubation and then for 30 minutes every 1 hour during the days thereafter. Suspensions were centrifuged, and the supernatant analyzed for P. Phosphorus that disappeared from the solution was considered to have been sorbed by the samples.

Data obtained on P sorbed by soils (Q) and equilibrium P concentrations (C) were fitted to the following sorption equations:

The Freundlich equation:

$$Q = KC^{1/n} \tag{4.1}$$

where K and n are constants. The estimated constant K may be considered an index of P sorbed from a solution, and may thus provide an estimate of relative P sorption capacity of different soils (Biggar & Cheung, 1973; Sanyal et al., 1993).

The Langmuir equation:

$$Q = \frac{aQ_mC}{1 + aC} \qquad (4.2)$$

where Q_m and a are constants. Q_m is designated as the Langmuir sorption maximum, and a is related to binding energy; and

The Tempkin equation (Hayward and Trapnell, 1964):

$$Q = a + k\ln(C) \qquad (4.3)$$

where a and k are constants. The equation is derived from the assumption that the affinity term decreases linearly as the amount of sorption increases.

A control experiment was set up to determine aggregate recovery. Twenty grams of each fraction of aggregates were equilibrated with 200 ml P-free 0.001 *M* $CaCl_2$ solution for 6 days. At the end of incubation, the solution was discarded and aggregates were air-dried and separated into the original size fractions. The aggregate recovery, the ratio of the weight recovered of each fraction to the initial weight, was over 96 %.

Phosphorus Sorption Kinetic Experiment

Two grams of each aggregate fraction were reacted with 20 ml 0.001 *M* $CaCl_2$ solution containing P 27.51 mg L^{-1} for 1, 2, 4, 8, 24, 72, 144 hours at 298° K with two replicates. At the end of each period, the contents of the containers were centrifuged and P was measured in the supernatant. The data were fit to several equations: the parabolic diffusion equation, power function, Elovich equation, and apparent first-order equation. A conceptual diffusion model with P reaction with soils was also considered.

Data obtained on P sorbed by aggregates (Q) and reaction time (t) were fitted to the following equations:

The power or modified Freundlich equation:

$$Q = kt^{v} \tag{4.4}$$

where k and v are constants and v is usually positive and smaller than one. This expression is generally considered empirical, but has been extensively used to represent the kinetics of chemisorption (Bangham & Burt, 1924) and is often known as the Bangham equation.

The parabolic equation:

$$Q = kt^{1/2} \tag{4.5}$$

This equation is a special case of equation (4.4) when the constant v is 0.5. It is generally considered to provide evidence that the rate determining step is, somehow, a diffusion process. A modified form of the equation, however, is often used in literature (Vig and Dev, 1979; Raven and Hossner, 1994; Allen et al., 1995), probably due to fitting the equation to data:

$$Q = a + kt^{1/2}$$

The Elovich equation:

$$Q = a + (\frac{1}{b})\ln(t) \tag{4.6}$$

where a and b are constants. It has been employed with apparent success by a number of workers for representing the kinetics of P sorption and release from soils.

The apparent first-order equation:

$$Q = Q_m(1 - \alpha\exp(-\beta t)) \tag{4.7}$$

where Q_m is the amount sorbed at $t \rightarrow \infty$ estimated by the nonlinear regression procedure, and α and β are constants. Equation (4.7) is an integrated form of

$$\frac{dQ}{dt} = \beta(Q_m - Q) \tag{4.8}$$

The apparent first-order equation is indistinguishable from a true first-order equation when Q_m is independent of the concentration of sorbate in solution and $\alpha = 1$. It has been used by numerous researchers to describe time-dependent data (Spark, 1989).

The Diffusion Model

A diffusion model has been proposed to describe the kinetics of P sorption and release in soils (Pavlatou and Polyzopoulos, 1988; Aharoni et al, 1991). The model assumes that the rate-limiting step is probably a transport process taking place in the liquid, such as diffusion in the bulk liquid, through the film adjacent to the solid particle, in liquid-filled pores, etc (Aharoni, et al., 1991). However, their model did not consider the effect of P sorption on P concentration, and thus diffusion.

The diffusion equation for a non-adsorbed ion

$$\theta \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} \qquad (4.9)$$

where C is concentration, x a space coordinate, and θ the volumetric moisture content of soil. D_e is the effective diffusion coefficient in the soil ($D_e = D_L f$, where D_L is the diffusion coefficient in water, *f* is the tortuosity or impedance factor for the solute in the soil).

When ion diffusion is accompanied by sorption, the usual equation for diffusion has to be modified to allow for this according to Crank (1975) and Jury et al. (1991)

$$\theta \frac{\partial C}{\partial t} = D_e \frac{\partial^2 C}{\partial x^2} - \rho_b \frac{\partial C_s}{\partial t} \qquad (4.10)$$

where ρ_b is the bulk density of soil. For simplification, let the amount sorbed be linearly related to the concentration in solution by a multiplier β (buffer coefficient) so that $C_s = \beta C$. Substitute this equation into equation (4.10) and rearrange:

$$\frac{\partial C}{\partial t} = D_e/(1 + \rho_b\beta/\theta)\frac{\partial^2 C}{\partial x^2} \qquad (4.11)$$

An estimate of the effective diffusion coefficient (D_e) for a sorbed ion in the soil is

$$D_e = D_L f/(1 + \rho_b\beta/\theta) \qquad (4.12)$$

In order to estimate D_e in equation (4.12), tortuosity factor *f* and P buffer coefficient β must be estimated. The tortuosity factor is a ratio of the diffusion coefficient for non-reactive solutes in soil to the diffusion coefficient of the solutes in free water ($f = D_e/D_L$). For bulk soils, a value from 0.2 - 0.3 has been reported (Pinner and Nye, 1982; Darrah, 1991; Collis-George and Geering, 1993; Hatano et al., 1993). The impedance factor for P movement in intra-aggregate pores, however, is difficult to determine reliably (Nye and Staunton, 1994). In this experiment, the value of 0.001 reported by Nye and Staunton (1994) was used for estimating the D_e of P in intra-aggregate pores.

Phosphorus buffer coefficients β were determined using the P sorption data at the reaction period of 1 day. A short equilibration time was chosen to minimize the effect of P diffusion into the aggregates on estimating β. Phosphorus sorption at 1 day was over 95% of P sorption at 6 days (data not shown).

Equation (4.11) should be applied to P sorption in the soil with caution because P sorbed is not linearly related to P concentration in solution as shown in most isotherm studies. In practice, fertilizer P applied to the soil is, however, usually small, thus P concentration in soil solution is relatively low, probably less than 1 mg P L^{-1} for high P fixation soils. For low concentrations the linear relationship between sorbed P and P concentration in soil should be a reasonable approximation.

Statistical Analysis

Goodness of fit of P sorption and kinetic equations to the data was evaluated with coefficients of determination (r^2) and the standard error (Se) of regression equation between Q_o and Q_p. Se is defined as

$$Se = \sum \frac{(Q_o - Q_p)^2}{n - p} \tag{4.13}$$

where n, Q_o, and Q_p are the number of observations, the observed and predicted sorption quantity, respectively, and p is the total number of model parameters including an intercept.

When it is desirable to compare alternative equations, a comparative measure of the goodness fit of each equation is required. Alternative equations were compared with the values of Se and r^2 in this experiment. A nonlinear procedure was used and approximate *t*-tests were constructed on coefficients according to standard statistical inference.

All data analysis were performed using S-PLUS (Statistical Science, 1995). The function `nls` in S-PLUS was used for the nonlinear equation fitting.

RESULTS AND DISCUSSION

The incubation studies with P added to a mixture of differing aggregate fractions (*Experiment I*), and separately to differing aggregate fractions (*Experiment II*) were used to evaluate changes in added P with aggregate size and incubation time. Phosphorus sorption, and extractable P by 0.001 *M* $CaCl_2$ and by 0.5 *M* $NaHCO_3$ will be reported. Extractable P in 0.001 *M* $CaCl_2$ solution estimated P in the soil solution while 0.5 *M* $NaHCO_3$ extractable P was used to assess available P, and includes both a port of P sorbed by aggregates and P in solution. The added P in each aggregate fraction was assumed to be P sorbed by aggregates because P in solution was very small (< 1% of the total P).

Incubation Experiment I (P Added to a Mixture of Aggregates)

1) Distribution of Sorbed Phosphorus among Aggregates

Figure 4.1 a shows the relationship between P sorbed in aggregate fractions and estimated surface area of aggregates after P was added to a mixture of differing aggregate fractions and incubated for 28 days (*Experiment I*). Phosphorus sorption in aggregates increased as the surface area of aggregates increased from 1 to 8 m^2 kg^{-1} (the corresponding aggregate diameter from 5.1 to 0.78 mm). The subsequent change in sorbed P with further increase in the surface area was small (Figure 4.1a). At 473 mg P kg^{-1}, for example, P sorption in aggregates increased from 273 to 551 mg P kg^{-1} as aggregate diameter decreased from 5.1 to 0.78 mm (estimated surface areas from 1 to 8 m^2 kg^{-1}), and only an additional 115 mg P kg^{-1} when aggregate diameter decreased to 0.32 mm (19 m^2 kg^{-1}).

The results are consistent with previous findings that P was initially sorbed to the surface of soil aggregate (Linquist et al., 1997), ferrihydrite particles (Willet et al., 1988), and synthetic aggregates coated with amorphous Fe (Gunary et al., 1964). Figure 4.1a, however, indicates that increased outer surface area of aggregates alone did not account for the difference in sorbed P among aggregate fractions. It is expected that the change in sorbed P with surface area will be small in aggregate sizes less than 0.32 mm. Phosphorus was, therefore, assumed to be initially sorbed to a depth of 0.16 mm (the radius for the aggregate with diameter of 0.32 mm) around the periphery of aggregates based on the method of Linquist et al. (1997). Accordingly, the mass of soil in this outer

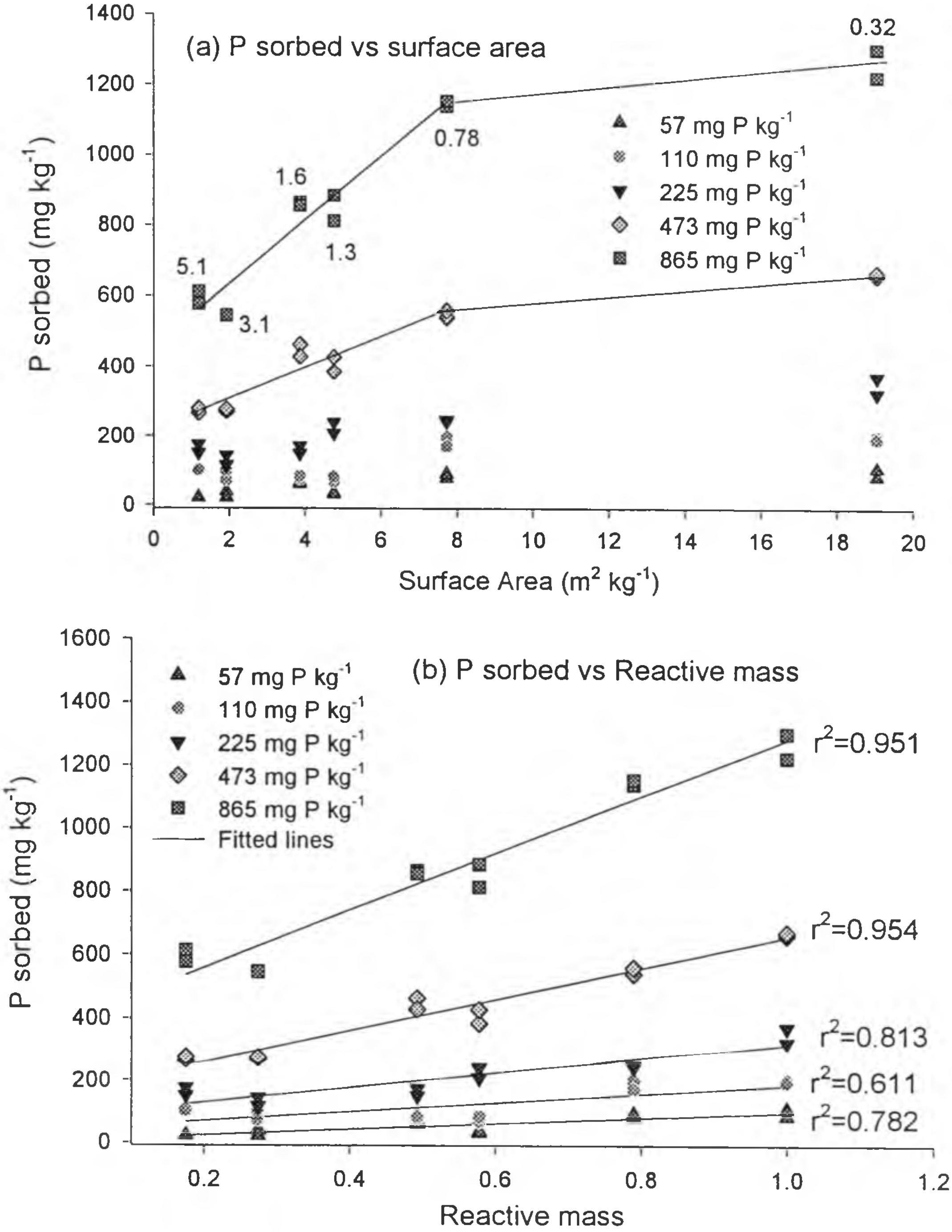

Figure 4.1. Relationships of P sorbed by aggregates to surface area and reactive mass. Phosphorus was added to a mixture of differing aggregate fractions of the Leilehua soil. The numbers beside the points in (a) are the volume weighted mean diameters. Two lines on (a) were drawn by hand to visualize the change in sorbed P in aggregates with aggregate size.

0.158 mm layer of the aggregate divided the total soil mass in the whole aggregates was defined as the *reactive mass* (kg kg^{-1}) (Linquist et al., 1997). The relationship between the sorbed P in aggregates and reactive mass was linear and highly significant ($p < 0.01$) as shown in Figure 4.1 b.

When P fertilizer is applied to a soil, a complex sequence of reactions follows. Phosphorus sorption presumably occurs after dissolution of P fertilizer takes place and P diffuses out of the fertilizer granule (Barrow, 1980). Phosphorus sorption is probably limited by the diffusion of P out of the fertilizer granule. The initial rapid P sorption observed in the laboratory studies may, therefore, not occur exactly the same in the field.

2) 0.001 *M* $CaCl_2$ Phosphorus

Extractable P by 0.001 *M* $CaCl_2$ decreased as aggregate size increased from size < 0.5 to 4 - 6 mm when P was added to the mixture of differing aggregate fractions (Figure 4.2 a & b), particularly, for the shorter incubation days. For the low P treatment of 473 mg P kg^{-1}, the small aggregate fraction (< 0.5 mm) contained 0.43 mg P kg^{-1} soil, and the large aggregate fraction (4-6 mm) less than 0.1 mg P kg^{-1} soil. For the high P level of 865 mg P kg^{-1}, the small and large aggregate fractions contained 8 and 3 mg P kg^{-1}, respectively. The increase in 0.001 *M* $CaCl_2$ extractable P with decreased aggregate size was probably due to an increase in the sorbed P in aggregates. Phosphorus concentration in the soil solution should, however, be the same for all aggregate fractions after P was added to the mixture. Thus the decrease in 0.001 *M* $CaCl_2$ extractable P with

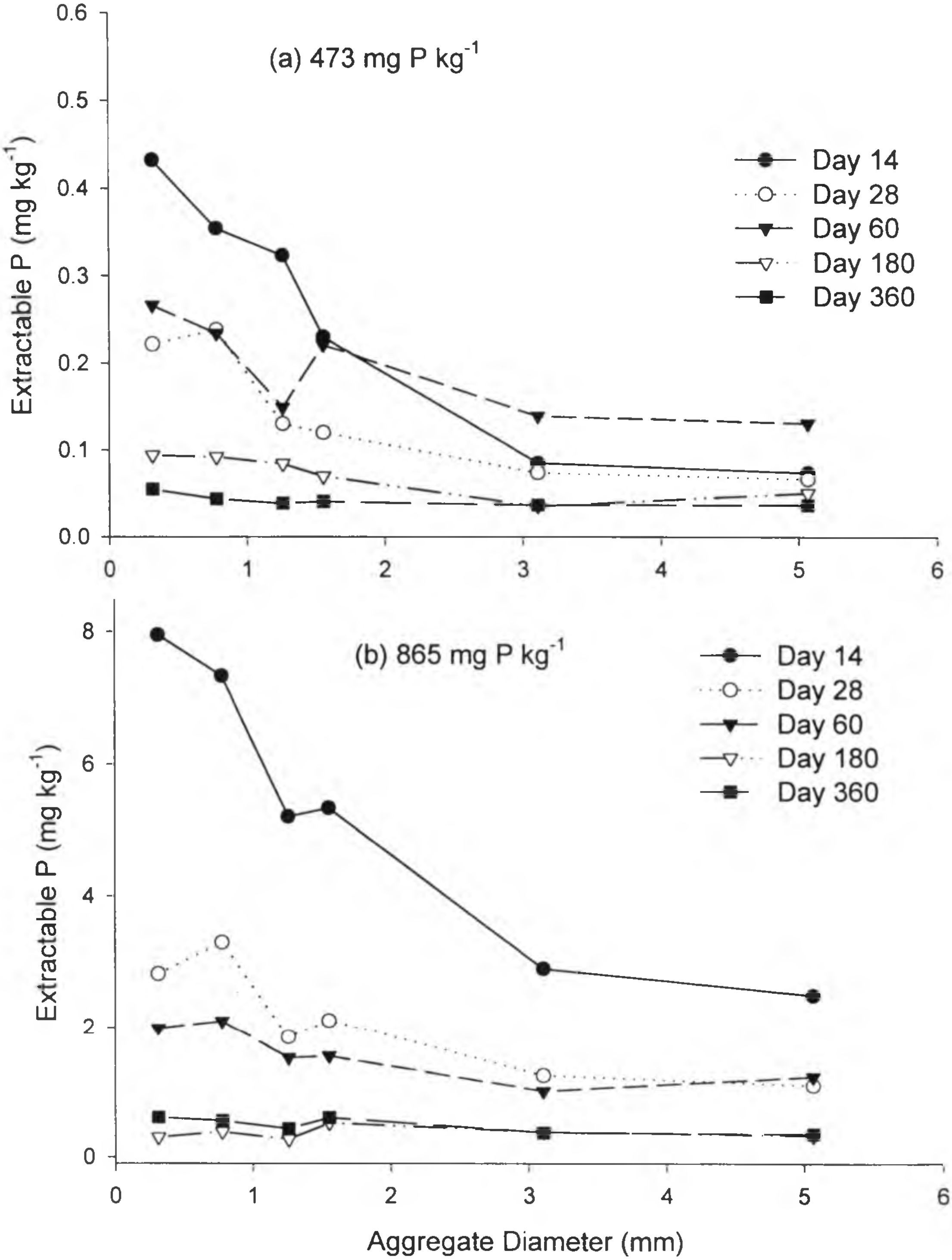

Figure 4.2. Changes in 0.001 *M* $CaCl_2$ extractable P with aggregate diameter at different incubation periods. Phosphorus was added to a mixture of differing aggregates on the Leilehua soil.

increasing aggregate size suggests that P re-adsorption probably occurred during the extraction due to breakup of aggregates and exposure of more reactive sites to solution. The magnitude of this subsequent P sorption for large aggregates was greater than that for small aggregates, possibly because more internal unoccupied sorption sites on large aggregates were exposed to solution.

The change in 0.001 M $CaCl_2$ extractable P with time is shown in Figure 4.3. There was a rapid decrease in solution P within the 30 day incubation, followed by a small decrease between 30 and 180 days, and a very small change after the incubation for 180 days. The curves converged at the 360 day incubation. Both the slow reaction of P with soil components and P redistribution among aggregates are probably the factors that influence the changes in solution P with time and aggregates size. The possible redistribution of added P among aggregates may be the reason that the decrease in solution P in small aggregate fractions was larger than that in large aggregate fractions.

3) 0.5 *M* $NaHCO_3$ Phosphorus

Phosphorus extracted by 0.5 *M* $NaHCO_3$ from aggregates separated after incubation decreased as aggregate sizes increased from size < 0.5 to 4 - 6 mm during the incubation period of 360 days (Figure 4.4 a-f). For example, with P application of 110 mg P kg^{-1} to the mixture, subsequently separated aggregate fractions with sizes of 4 - 6 and < 0.5 mm contained approximately 13 and 27 mg P kg^{-1} soil, respectively, at the 14 day incubation (Figure 4.4 c). With P application of 865 mg P kg^{-1}, a range of 120 to

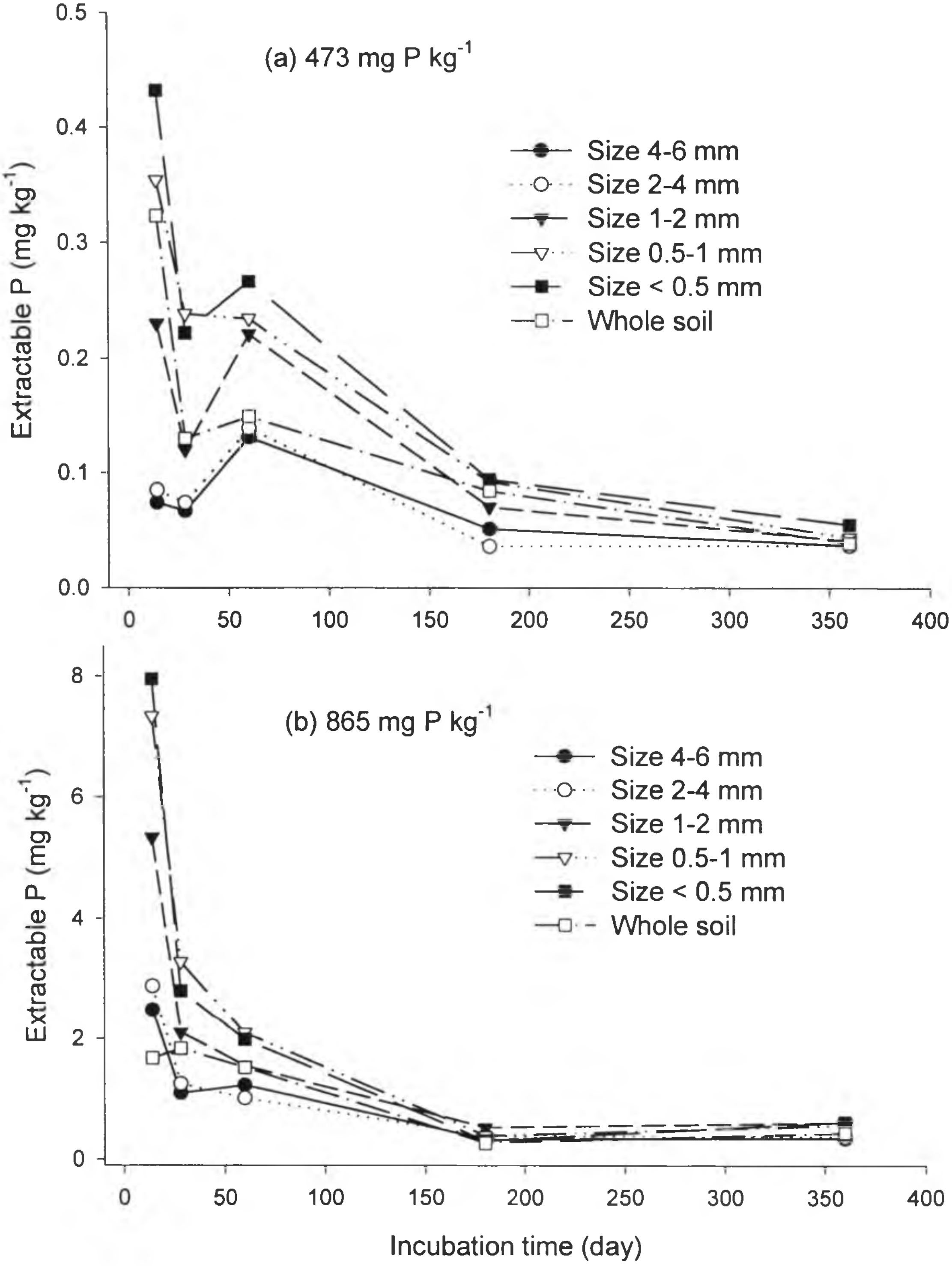

Figure 4.3. Changes in 0.001 *M* $CaCl_2$ extractable P with time for differing aggregates on the Leilehua soil.

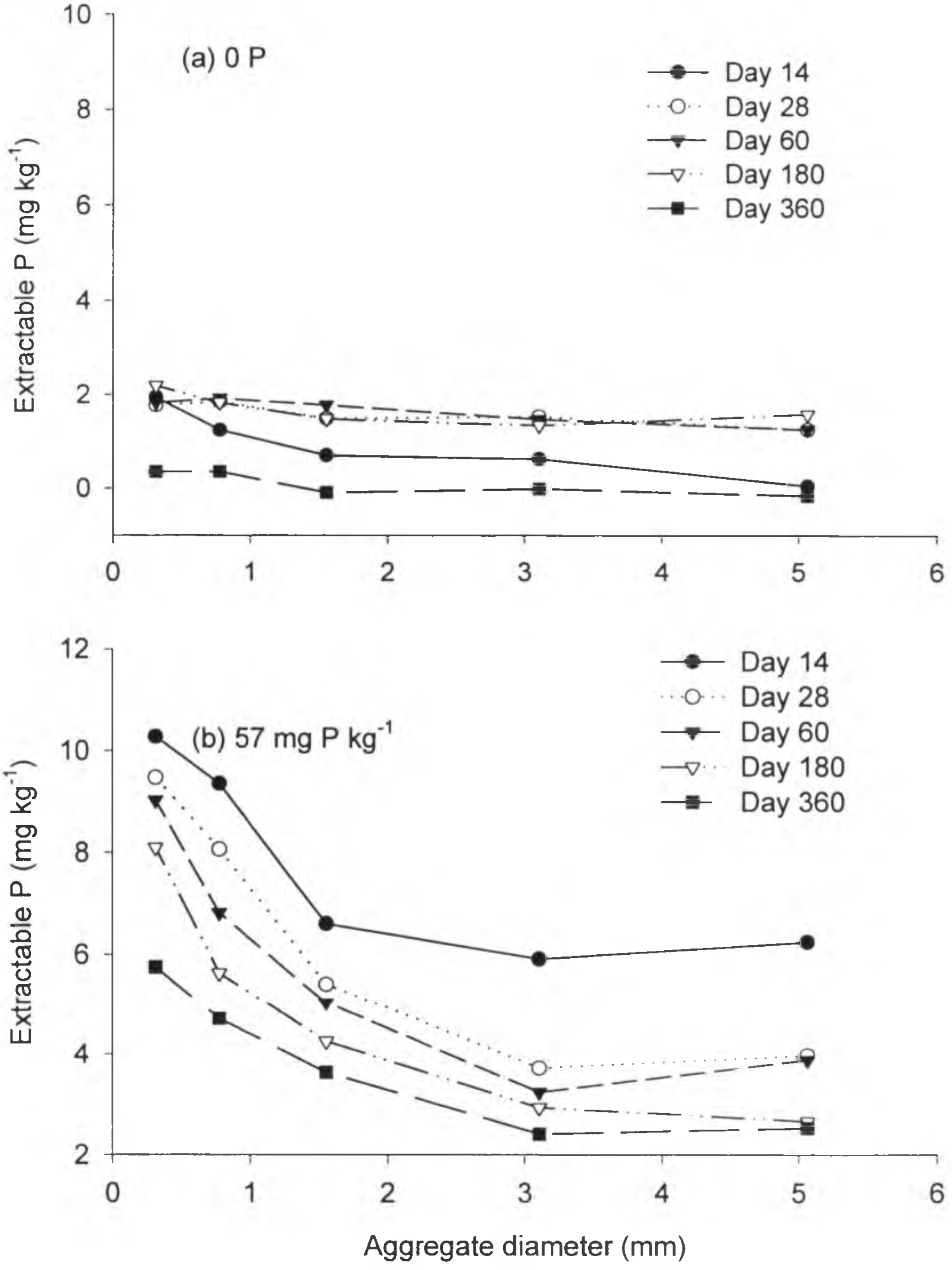

Figure 4.4. Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate diameter at different incubation periods. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

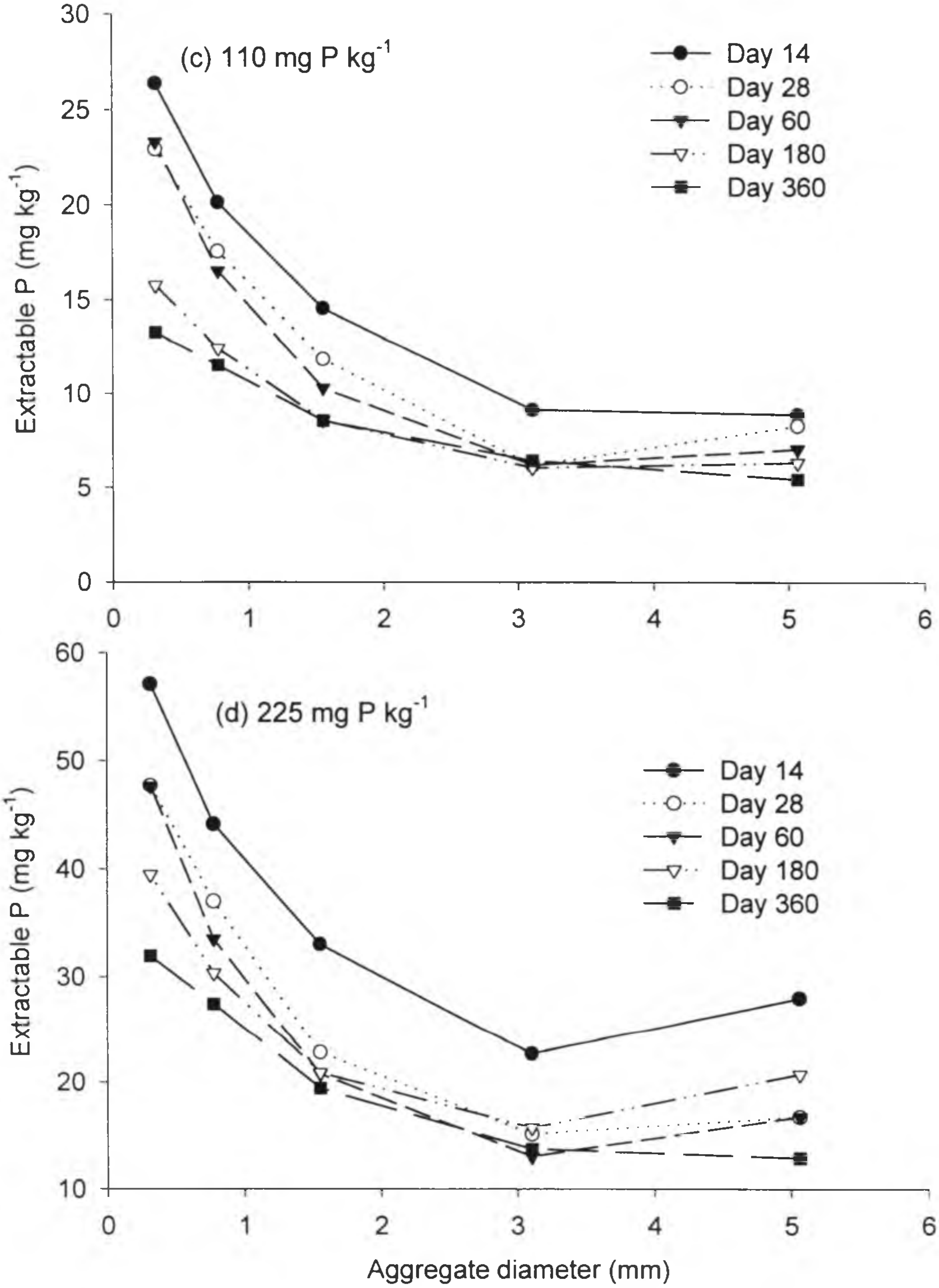

Figure 4.4 (Continued). Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate diameter at different incubation periods. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

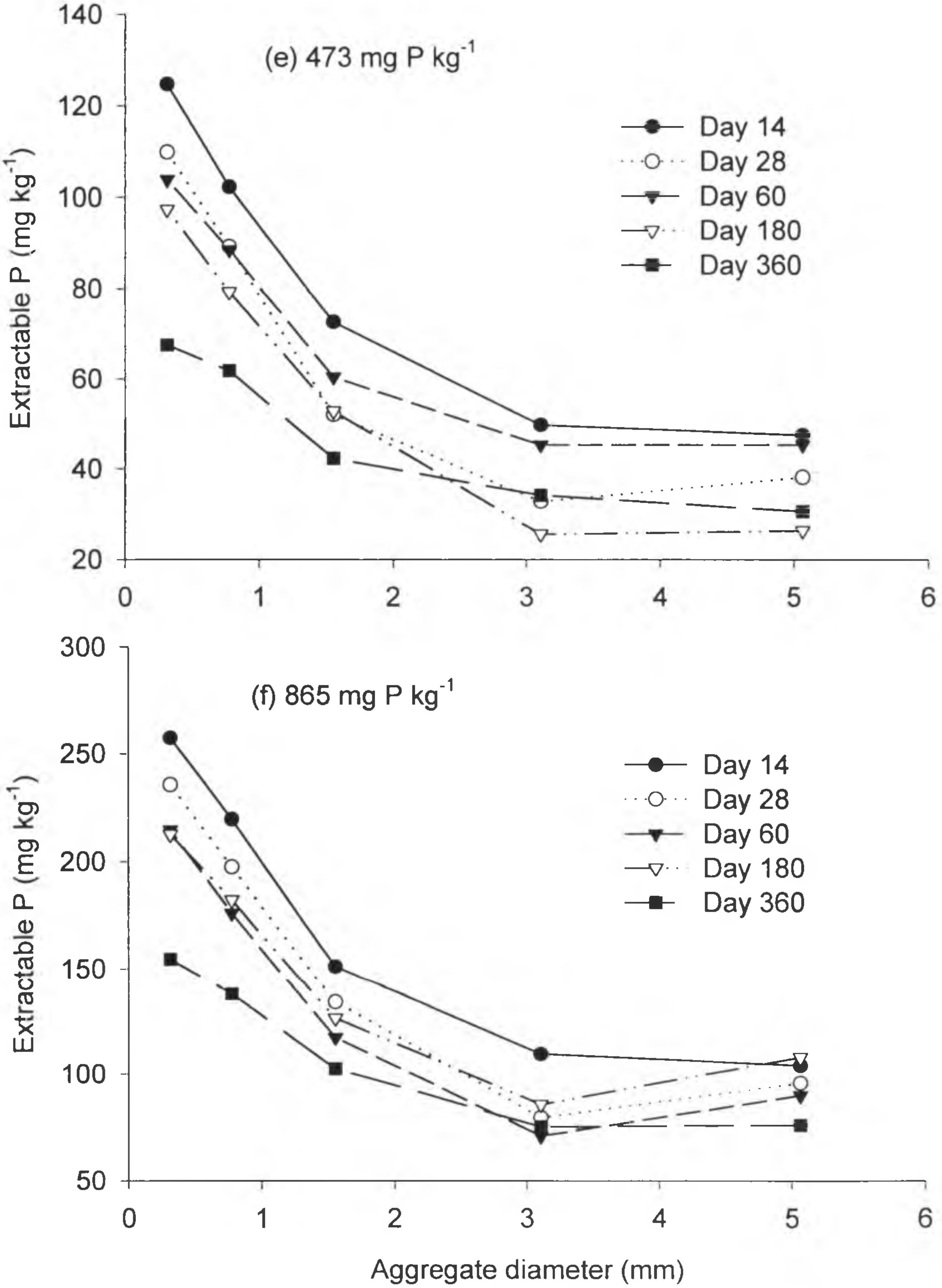

Figure 4.4 (Continued). Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate diameter at different incubation periods. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

270 mg P kg^{-1} of extractable P in the corresponding aggregates was observed (Figure 4.4 f). The decrease in 0.5 *M* NaHCO3 extractable P with increased aggregate size was consistent with the change in sorbed P in aggregates. For shorter incubation periods, a similar pattern of decreasing 0.5 *M* $NaHCO_3$ extractable P with increasing aggregate size was found, with exception that extracted P frequently was higher for the 4-6 mm aggregate fraction than for the 2-4 mm aggregate fraction.

With increased incubation time, extractable P decreased for all subsequently separated aggregate fractions studied at all P levels (Figure 4.5 a-f) after P was added to the mixture of aggregate fractions. The decrease in extractable P with time can be divided into two stages: 1) a fast decrease during 28 days of incubation, and 2) a slow decrease between 28 and 360 days of incubation. The results suggested that extractable P continued to decrease after the incubation of 360 days, particularly for smaller aggregate fractions.

The decrease in extractable P with time for small aggregate fractions was greater than that for large aggregate fractions. The slow reaction of P with soil components, which probably accounted for the decrease in solution P, probably does not explain the decrease in 0.5 *M* $NaHCO_3$ extractable P with time because 99% of the added P was no longer in solution as measured by 0.001 *M* $CaCl_2$. Thus the decrease in 0.5 *M* $NaHCO_3$ extractable P may not be due to more solution P being sorbed to the solid phase (aggregates). The probable reasons may include increasing binding between sorbed P and soil components, or changing into insoluble compounds with incubation time.

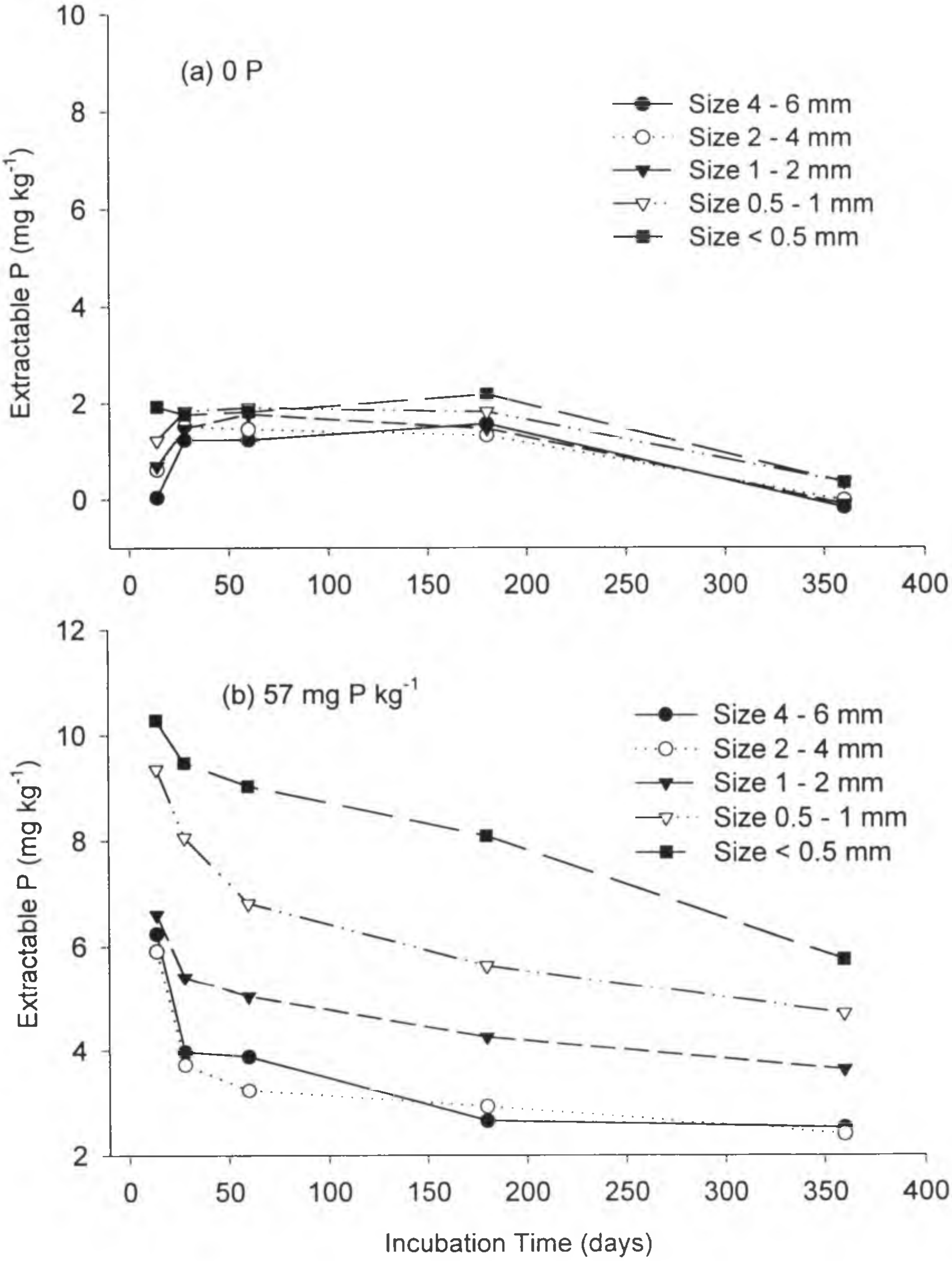

Figure 4.5. Changes in 0.5 *M* $NaHCO_3$ extractable P with time for various aggregate fractions. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

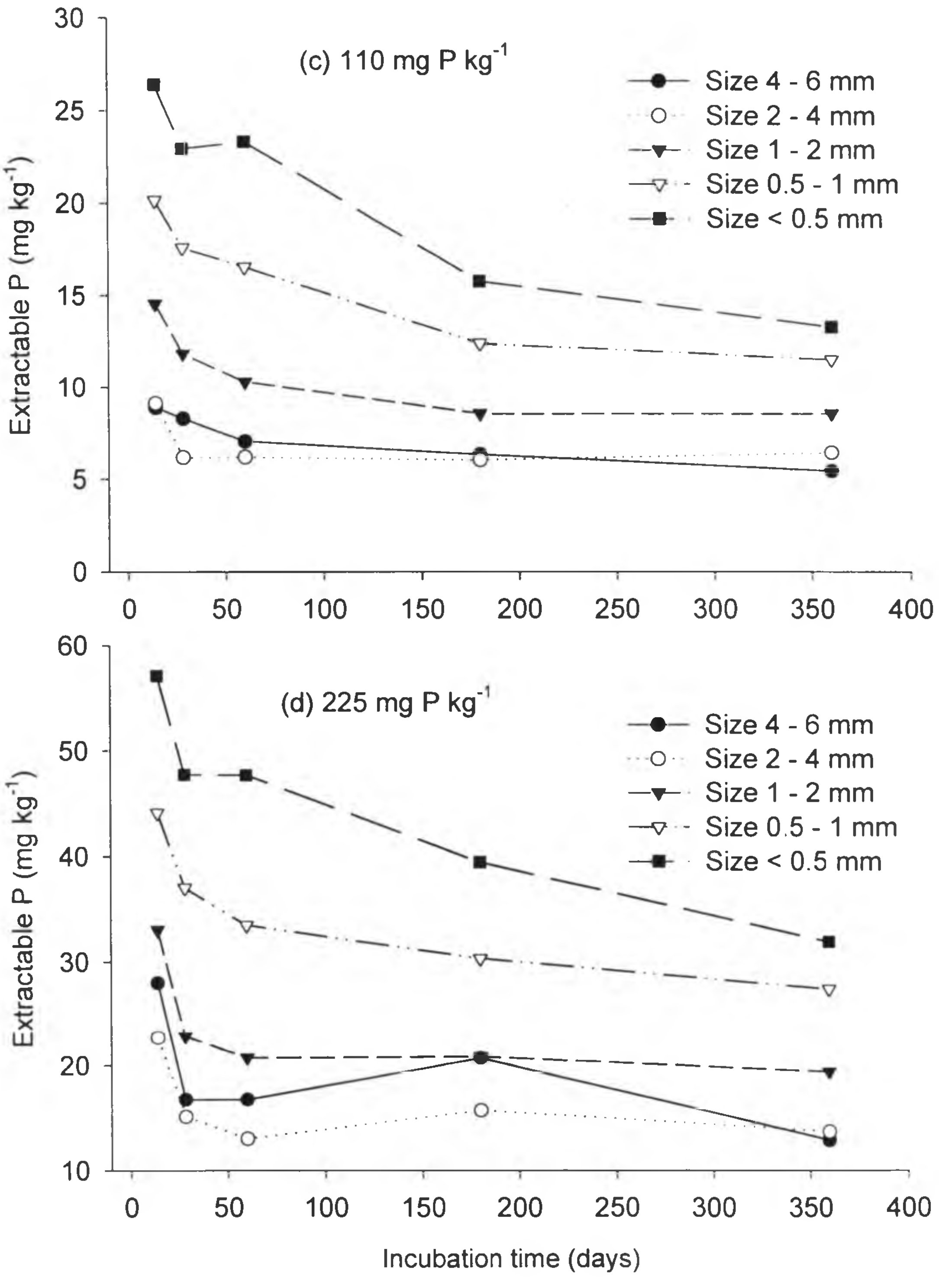

Figure 4.5 (Continued). Changes in 0.5 *M* $NaHCO_3$ extractable P with time for various aggregate fractions. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

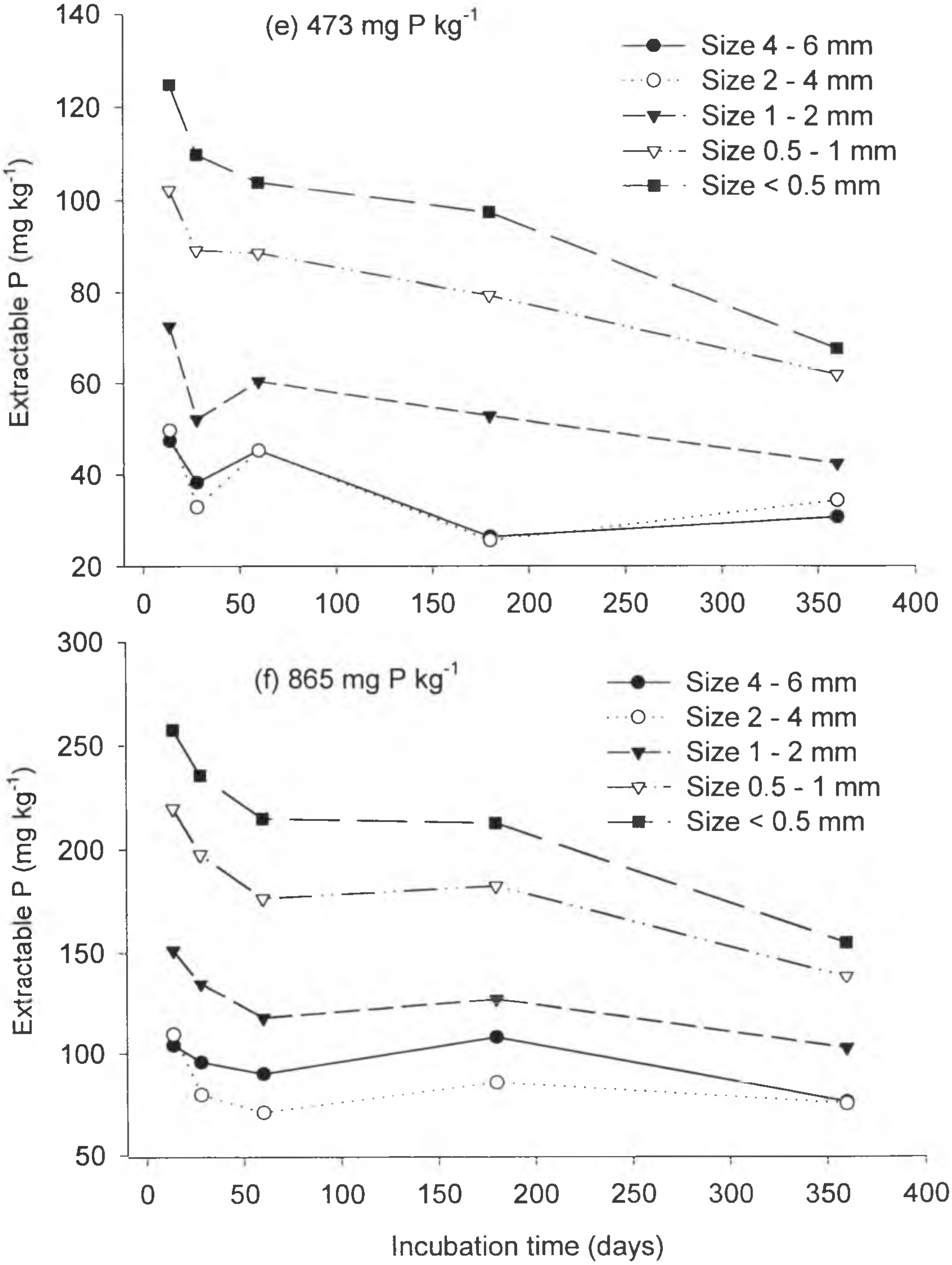

Figure 4.5 (Continued). Changes in 0.5 *M* $NaHCO_3$ extractable P with time for various aggregate fractions. Phosphorus was incubated with a mixture of aggregates on the Leilehua soil.

Another factor may be the redistribution of sorbed P among aggregates due to the diffusion of P between and into aggregates, and to soil mixing. In the field, aggregate size and fertilizer mixing with soil are probably influenced by plant root penetration, tillage, and microorganisms. These factors may play an important role in controlling distribution of applied P among aggregate fractions.

Incubation Experiment II (P Added to Separated Aggregates)

1) Phosphorus Sorption

The relationship between the sorbed P in aggregates and P concentration in 0.001 M $CaCl_2$ solution could only be fitted to the Tempkin equation based on coefficients of determination and the standard error (Figure 4.6 a). The Freundlich and Langmuir equations did not fit the P sorption data very well (data not shown). The sorbed P and P buffer coefficient (the first derivative) at 0.2 mg P L^{-1} in solution ($PS_{0\,2}$ and $PBC_{0\,2}$, respectively) were estimated from the Tempkin equation. The values of $PS_{0\,2}$ increased from 434 to 526 mg P kg^{-1}, and $PBC_{0\,2}$ from 718 to 1018, respectively, as aggregate size decreased from 4-6 to <0.5 mm. The relationships of $PS_{0\,2}$ and $PBC_{0\,2}$ to reactive mass were linear and highly significant ($p < 0.01$) as shown in Figure 4.6 b.

2) 0.001 M $CaCl_2$ Extractable Phosphorus

When phosphorus was added to separated aggregate fractions, solution P estimated from 0.001 M $CaCl_2$ extractable P increased with increased aggregate size

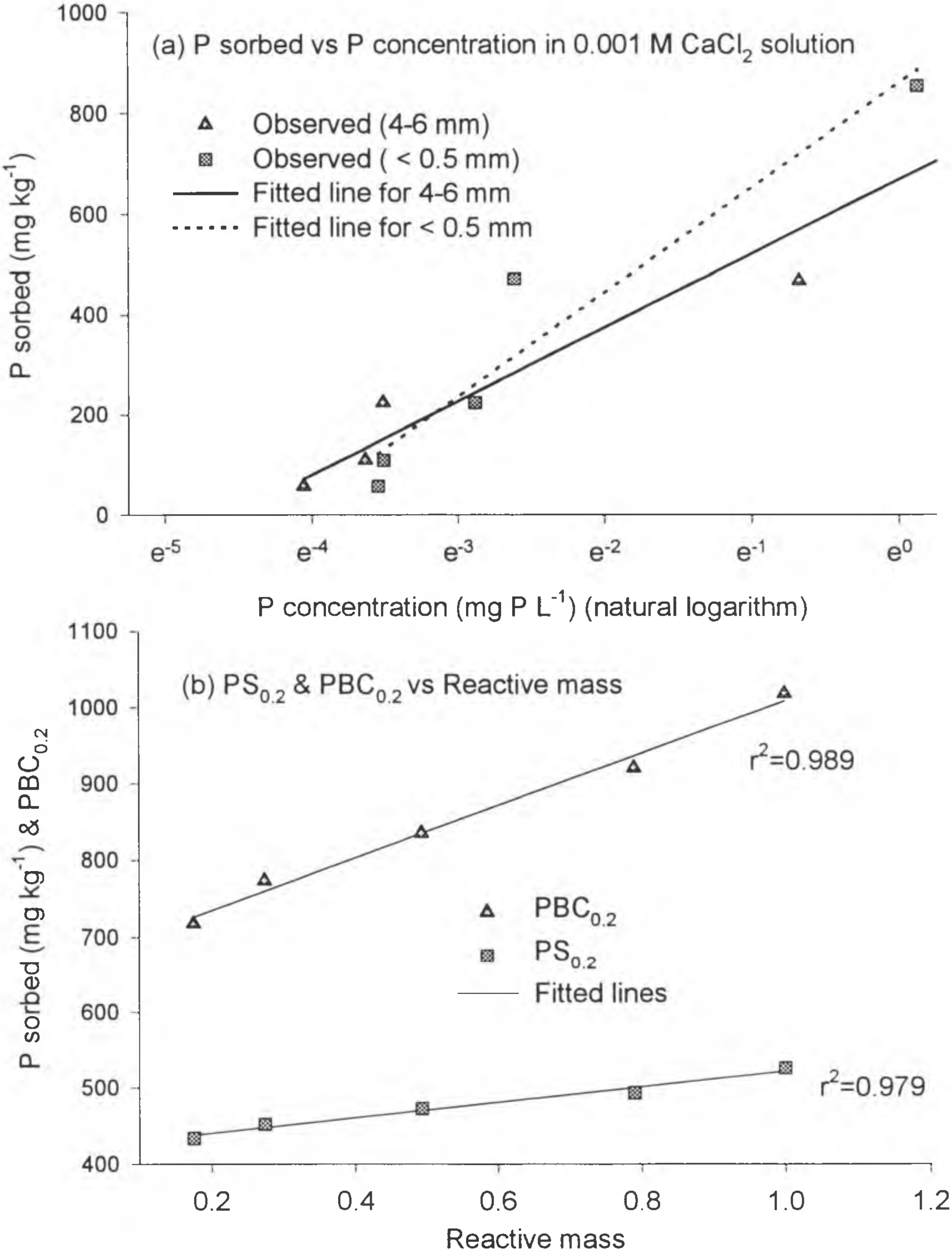

Figure 4.6. (a) Phosphate sorbed as a function of P concentration after 28 day incubation of separated aggregates. (b) Relationships of P sorption and P buffering cofficient at solution P 0.2 mg L^{-1}($PS_{0.2}$ & $PBC_{0.2}$) to reactive mass.

(Figure 4.7). If P sorption is mainly influenced by the outer surface area of aggregates for a given soil, it follows that small aggregate fractions, with greater surface area, should sorb more P than large aggregate fractions after the same amount of P is added to separated aggregate fractions. Thus solution P for small aggregate fractions will be less than that for large aggregate fractions because more of the added P should be sorbed by small aggregate fractions. Our results support this hypothesis.

The continuous reactions between 0.001 *M* $CaCl_2$ extractable P and aggregates are shown in Figure 4.8 after P was added to separated aggregates. The 0.001 *M* $CaCl_2$ extractable P in aggregates by the 36 hour equilibrium was greater than extractable P by the 8 day equilibrium. The 0.001 *M* $CaCl_2$ extractable P by shaking aggregates 15' was within the range of the 36 hour equilibrium and 8 day equilibrium methods. The decrease in 0.001 *M* $CaCl_2$ extractable P from large aggregates with increased equilibrium time was greater than that from small aggregates. This suggests that more P re-adsorption occurred for large aggregates than for small aggregates.

3) 0.5 M NaHCO3 Extractable Phosphorus

Changes in 0.5 *M* $NaHCO_3$ extractable P with aggregate size were dependent on the level of P addition after P was added to separated aggregate fractions for the incubation of 28 days (Figure 4.9). At lower P levels (0 -200 mg P kg^{-1}), extractable P increased as aggregate size increased from size < 0.5 to 4 - 6 mm. At higher P levels (400 and 800 mg P kg^{-1}), the change in extractable P with aggregate size was a U-shaped.

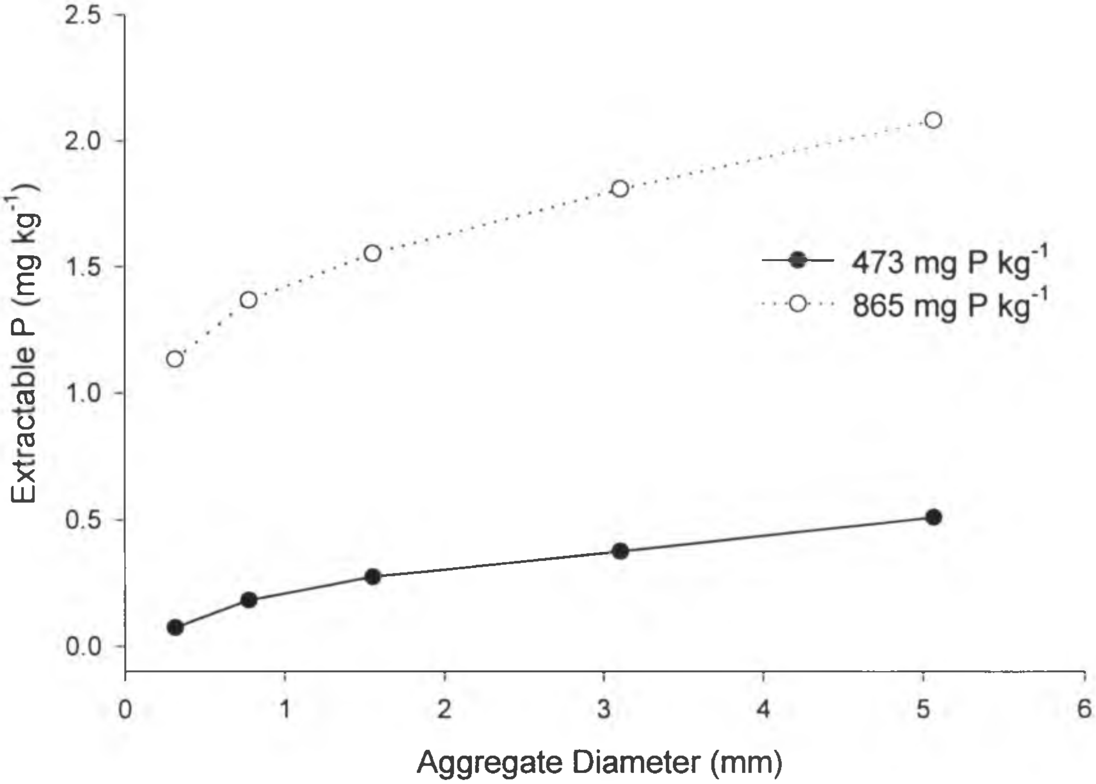

Figure 4.7. Change in 0.001 *M* $CaCl_2$ extractable P with aggregate diameter. Phosphorus was added to separated aggregates for the 28 day incubation on the Leilehua soil.

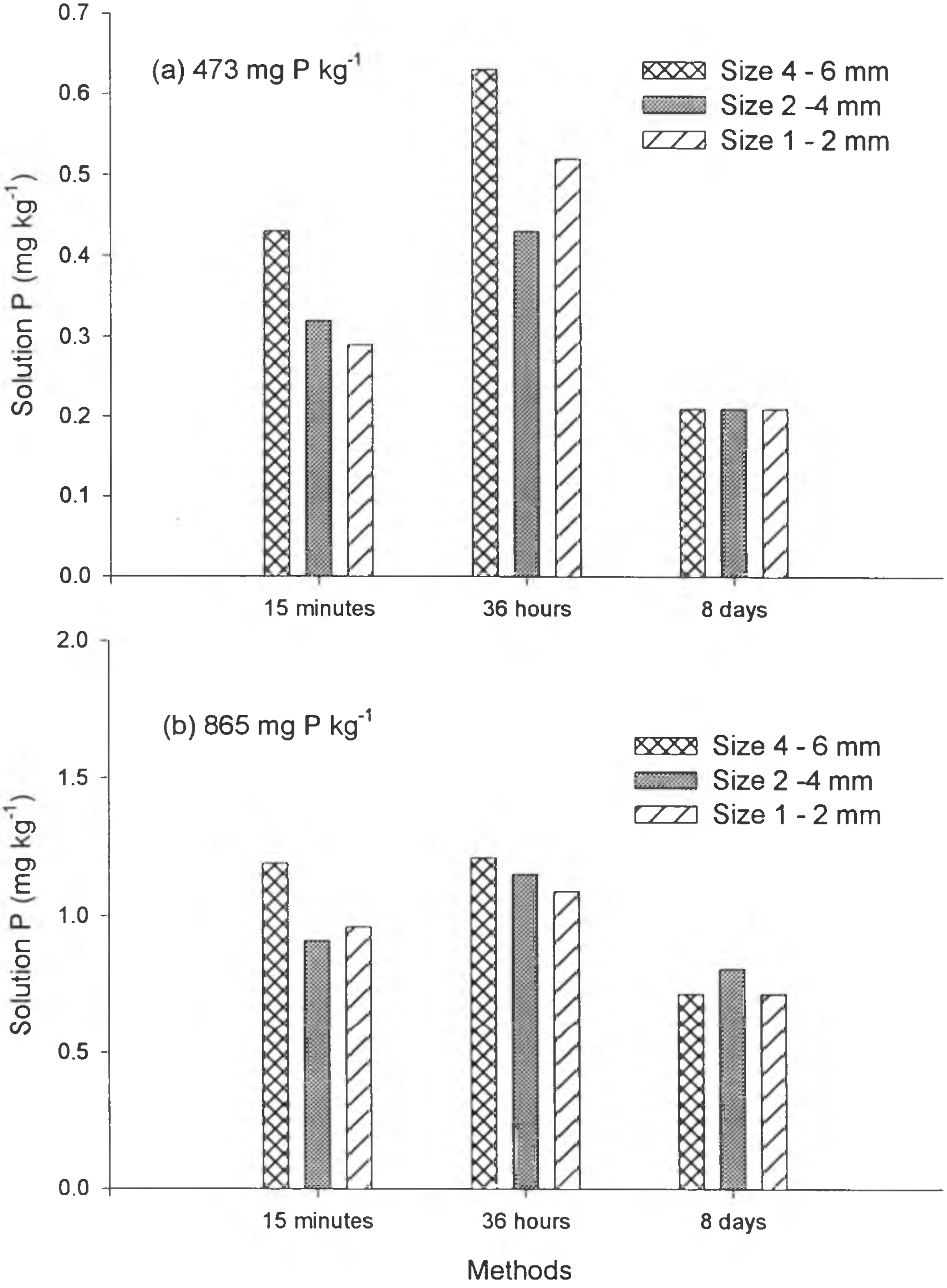

Figure 4.8. Differences in 0.001 *M* $CaCl_2$ extractable P as measured with three different methods for the Leilehua soil.

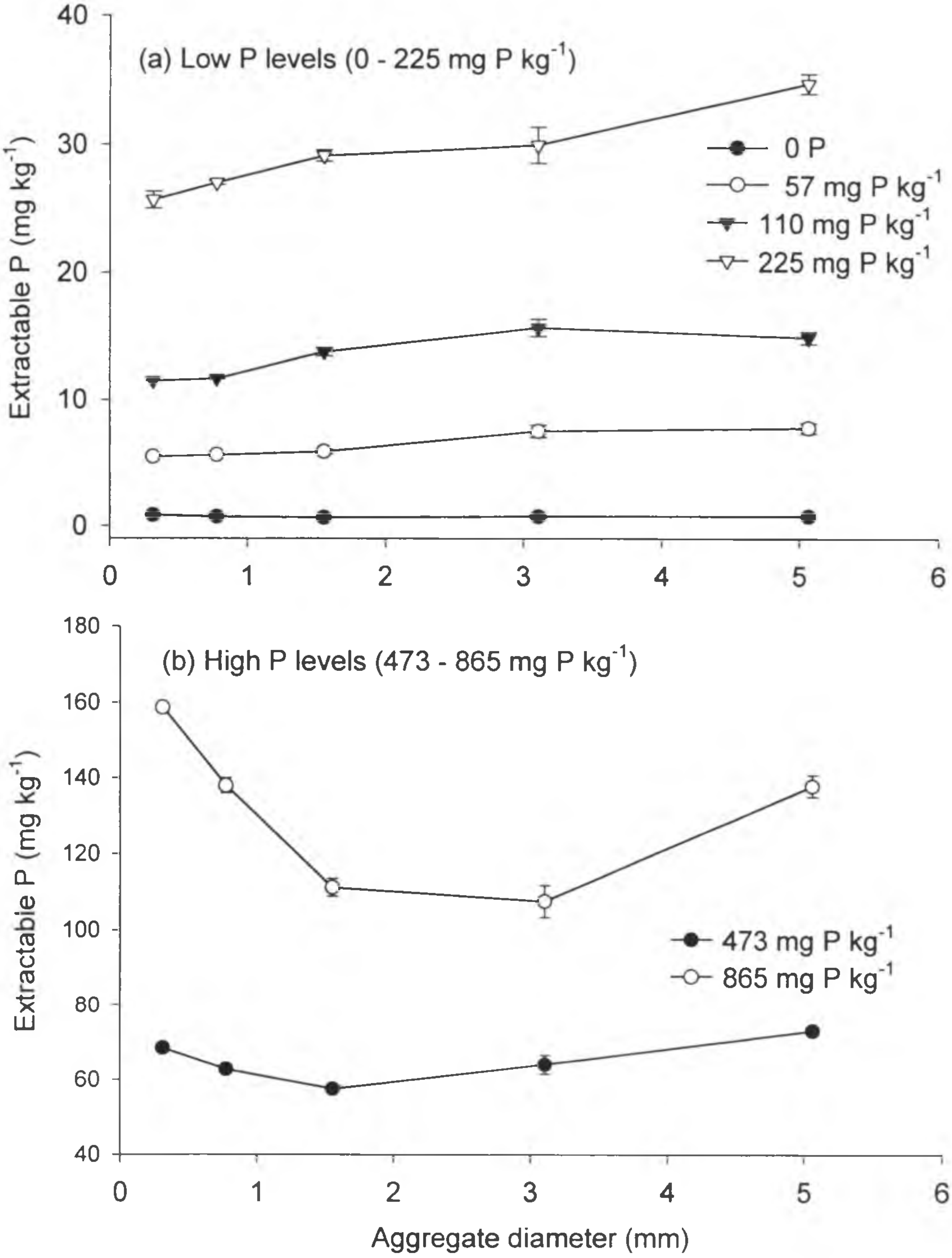

Figure 4.9. Changes in 0.5 *M* $NaHCO_3$ extractabe P with aggregate diameter after P was added to separated aggregates for 28 day incubation for the Leilehua soil. Error bars represent one standard error. Symbol size may exceed error bars in some cases.

Extractable P was the lowest at the aggregate size between 1-2 and 2-4 mm, and increased when the aggregate size became larger or smaller.

The effects of aggregate size on P extraction from soils are not clear yet, but several possible factors may influence P sorption and desorption: (1) small aggregate size tends to increase P desorption. This is probably related to more sorption sites with sorbed P on the surfaces exposed to extracting solution; (2) large aggregate size tends to increase P desorption by decreasing P sorption due to less surface area in the first place; and (3) the affinity for P sorption decreases exponentially with increasing P saturation of the surface (Sposito, 1984). Thus more P will be in solution with increasing P addition, i.e. the curve for the relationship between desorbed P and P addition is concave upward. The measurement of extractable P probably reflects the combined effects of these factors.

In summary, the distribution of sorbed and extractable P among aggregates is probably the result of both the ratio of aggregate surface area to mass and the relatively low mobility of phosphorus. Generally, the rate of phosphorus reaction and sorption with soil components is much faster than P transport within and between aggregates. Most of the added phosphorus will, therefore, be distributed in the thin external layer of the aggregates. Because the surface area of small aggregates (per gram of soil) is larger than that of large aggregates, small aggregates will probably contain a larger amount of the added P than larger aggregates after P is added to mixtures of differing size fractions, thus more extractable P is measured in small aggregates.

The change in extractable P with aggregate size may be significant in fertilizer P management. It seems possible that aggregation and aggregate size could reduce P fixation, and increase P availability temporarily but not necessarily in the long term.

Modeling Changes in Extractable P in Aggregates

1) Phosphorus Buffering Coefficient

The changes in extractable P with aggregate size suggest that aggregate size probably influence the values of PBC. The P buffer coefficients were obtained from *incubation experiment II* after P was added to separated aggregates. The relationship between extractable P and P addition was not linear except for the 4-6 mm aggregates (Figure 4.10). The data can be described by two linear equations (in most cases, r^2 exceeded 0.999, data not shown) for simplification. The change of slope was visually estimated to occur at a P-addition of 200 mg kg^{-1}.

The relationship of PBC to reactive mass and aggregate size was modeled (*Experiment II*). Phosphorus buffer coefficients were related to aggregate diameter for P additions up to 200 mg kg^{-1}:

$$PBC = 0.1250 + 0.0093 * Diameter \quad (r^2{=}0.646,\ p{<}0.004) \tag{4.14}$$

Including reactive mass did not improve the prediction of PBC. For P additions between 200 and 800 mg kg^{-1}, PBC was highly significantly related to both aggregate diameter (Diameter) and reactive mass (ReactMass):

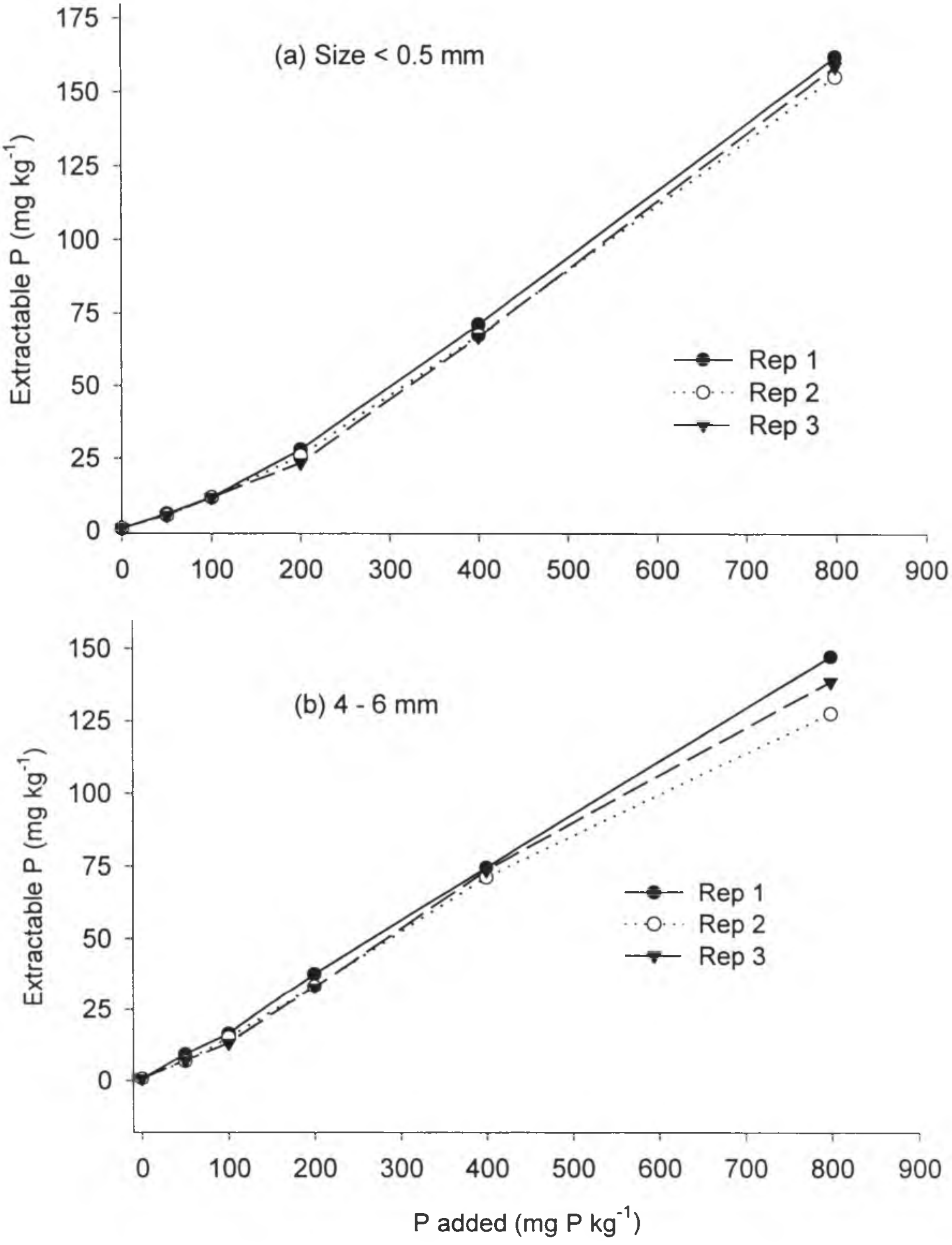

Figure 4.10. Relationship between 0.5 *M* $NaHCO_3$ extractable P and added P on the Leilehua soil. Phosphorus buffer coefficient (PBC) = extractable P/P added.

$$PBC = -0.0505 + 0.263 * ReactMass + 0.0350 * Diameter \ (r^2=0.924,\ p<10^{-6}) \qquad (4.15)$$

The 0.5 *M* $NaHCO_3$ extractable P in subsequently separated aggregate fractions was then predicted using PBC and the sorbed P in aggregates after P was added to the mixture of differing aggregate fractions *(Experiment I)*. A linear relationship between extractable P and added P was assumed:

$$P_{ext} = a + PBC * P_{add} \qquad (4.16)$$

where P_{ext} and P_{add} are extractable P from subsequently separated aggregates after P was added to the mixture (*Experiment I*) and the added P in these aggregates, respectively, and a is a constant, usually the extractable P in the unamended soil. For the Leilehua soil, this value is very small, with a mean of 1.67 mg P kg^{-1} (data not shown) for all aggregate fractions. The value of a = 1.67 mg P kg^{-1} was used in equation (4.16) for the prediction. P_{add} was estimated from the sorbed P in subsequently separated aggregates after P was added to the mixture of differing aggregate fractions (*Experiment I*), and was the differences of the total P between P-added aggregates and no P aggregates. The values of PBC were estimated using equation (4.14) and (4.15).

Predicted 0.5 *M* $NaHCO_3$ extractable P from equation (4.16) was compared with measured values (Figure 4.11). The predicted extractable P from PBC estimated by aggregate size and reactive mass was close to observed extractable P in aggregates. This

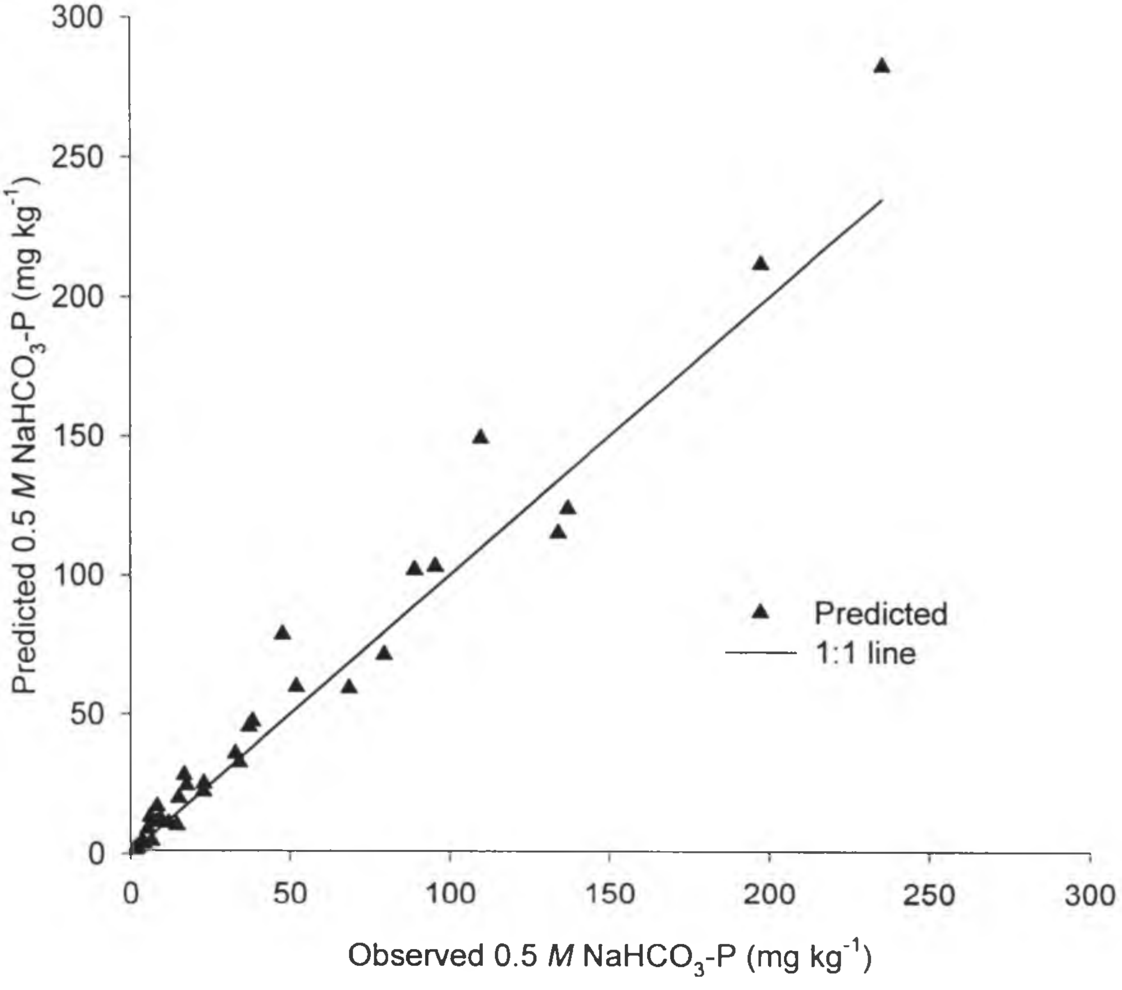

Figure 4.11. Comparison of measured P and P predicted by the equation $P_{ext} = a + PBC*P_{add}$ for the Leilehua soil. PBC = 0.1250 + 0.0093*Diameter for low P addition (0-200 mg P kg^{-1}), and for high P addition (200-800 mg P kg^{-1}), PBC = -0.0505 + 0.263*ReactMass + 0.0350*Diameter.

suggests that the influence of aggregate size and reactive on the values of PBC and the distribution of added P among aggregates should not be ignored.

2) Modeling Change in Extractable P with Aggregate Size and Time

Modeling P dynamics in aggregates with soil characteristics probably identify the effects of these characteristics on the P changes in soils and provide scientific information for P management. In the previous section, extractable P in separated aggregates from *Experiment I* was predicted from PBC (*Experiment II*) and added P in aggregates (*Experiment I*) using equation (4.16). With time, diffusion of sorbed P into and among aggregates probably occurs, and accordingly, the distribution of added P and extractable P among aggregates changes. In this section, PBC for subsequently separated aggregates (*Experiment I*) was related to aggregate diameter and reactive mass (similar to equation 4.15). The added P in separated aggregates was estimated based on the relationship between sorbed P in aggregates and reactive mass (Figure 4.1b). The decrease in extractable P with time was assumed to be exponential. Equation (4.16) may, therefore, be expanded to the following equation:

$$P_{ext} = b_{01} + (b_{02} + b_1 * Diameter + b_2 * ReactMass) * ReactMass * P_{add} * \exp(-b_3 * Time) \quad (4.17)$$

where P_{ext} is 0.5 *M* $NaHCO_3$-extractable P in subsequently separated aggregates, P_{add} is the P addition to the mixture of selected aggregate fractions, and Time is incubation period (days). b_{01}, b_{02}, b_1, b_2 and b_3 are constants.

The product of ReactMass and P_{add} was use to estimate the amount of added P in subsequently separated aggregate fractions. The sorbed (P_{sorbed}) in aggregate was highly significantly related to reactive mass and the levels of added P (P_{added}) in a mixture of aggregates:

$$P_{sorbed} = 1.6398 * ReactMass * P_{added} \qquad (r^2=0.960,\ p<10^{-16}) \qquad (4.18)$$

The factor ($b_{02} + b_1$*Diameter + b_2*ReactMass) was used to estimate the values of PBC. This factor initially contained a dummy variable to test whether the effect of reactive mass on PBC was dependent on P additions (0 - 200, and >200 mg P kg^{-1}). The coefficient of dummy variable was not significant at $p = 0.05$, and, consequently, the dummy variable was removed from the equation. The factor exp($-b_2$*Time) was used to estimate the decline in extractable P with time.

Extractable P in subsequently separated aggregates was modeled using equation (4.17) after P was added to the mixture of selected aggregate fractions (*Experiment I*). The data set was split into two data sets randomly, one for estimating parameters, and the other for cross validation of the equation. Table 4.1 shows the estimated coefficients, asymptotic inferences, and bootstrap confidence intervals based on 1000 bootstrap samples. The means of estimated coefficients by the bootstrap method were close to the means using the ordinary nonlinear regression method, but the confidence intervals were wider than the asymptotic confidence intervals. The confidence interval was estimated from the percentile of the bootstrap distribution of the coefficient (Efron and Tibshirani, 1993).

Table 4.1. Statistical summaries of coefficients of equation (4.17) based on model building data set[†].

	Ordinary nonlinear regression				Bootstrap inference		
	Value	Std. Error	t value	*p*	mean	LL[‡]	UL[‡]
b_{01}	-4.941	0.741	-6.6708	<0.001	-4.75	-5.58	-3.97
b_{02}	0.0490	0.0260	1.8874	0.03	0.025	-0.041	0.093
b_1	0.116	0.00720	16.063	<0.001	0.117	0.097	0.136
b_2	0.186	0.0260	7.1535	<0.001	0.219	0.154	0.286
b_3	0.000983	0.0000706	13.631	<0.001	0.001	0.0008	0.0011

[†] Data set of extractable P was split into two data sets, one for model building, the other for the cross validation.

[‡] LL, and UL are lower and upper limits of the confidence interval based on bootstrap percentile at $p = 0.05$ (B = 1000).

The prediction of extractable P in aggregates is illustrated in Figure 4.12. The predicted extractable P from aggregate size and reactive mass was close to observed values. This suggests that soil aggregate size was one of factors influencing the distribution of extractable P among aggregates. Consideration of the effect of aggregate size on PBC and P availability in P diagnosis may improve the prediction of P requirement. The influence of aggregate size on P desorption and P uptake by crops will be discussed in Chapter 5. Finally, the full data set was used to estimate the coefficients of equation (4.17) shown in Table 4.2. The standard errors of estimated coefficients by

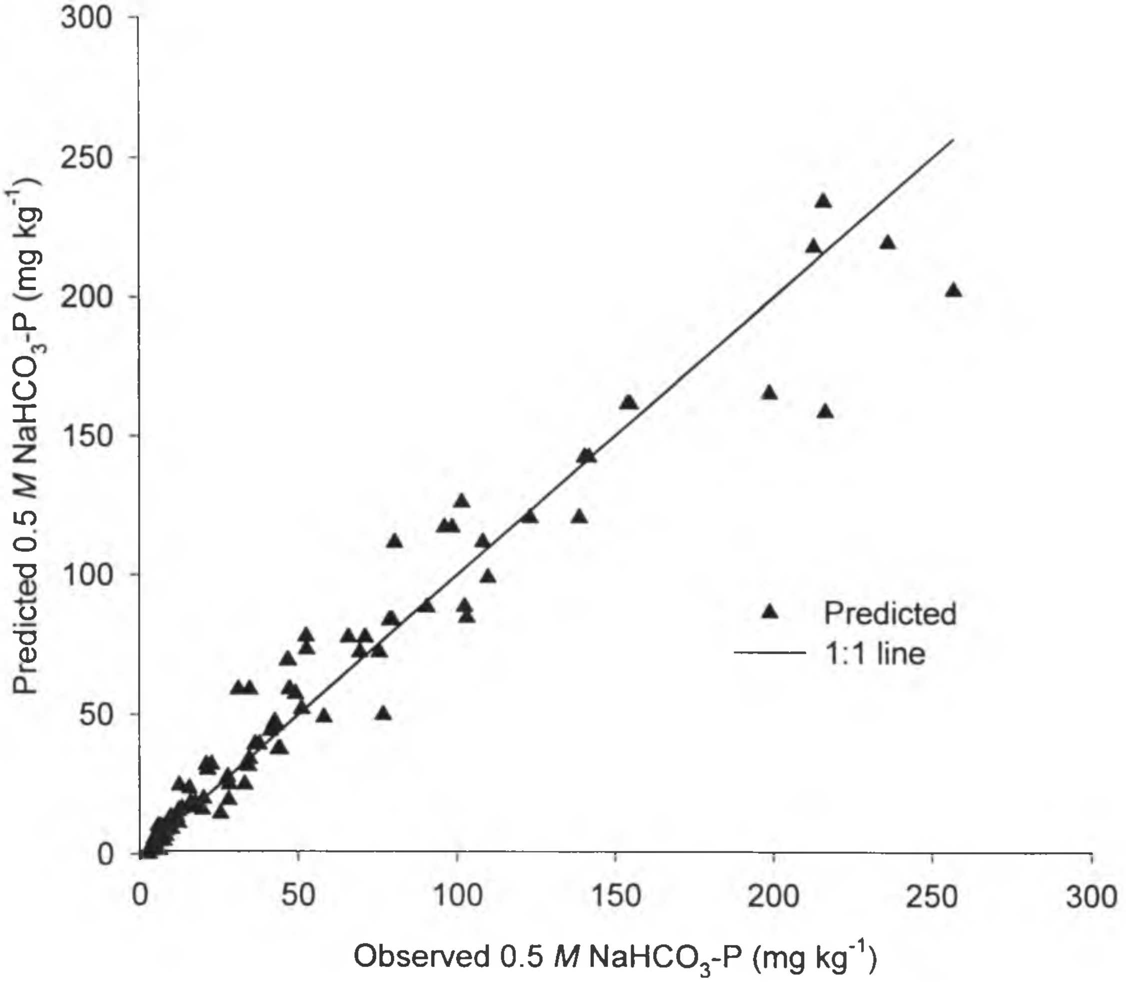

Figure 4.12. Comparison of measured P and P predicted by the equation for the Leilehua soil. The extractable P predicted from equation (4.17), and the observed values were from the cross validation dataset.

the bootstrap method were greater than those by the nonlinear regression procedure except for coefficient b_{01}.

Table 4.2. Statistical summaries of coefficients of equation (4.17) by the ordinary nonlinear regression procedure based on the full data set, and the standard errors by the bootstrap method.

Estimator	Value	Std. Error	t value	*p*	Se†
b_{01}	-4.81	0.620	-7.754	<0.001	0.426
b_{02}	0.0247	0.0217	1.140	0.13	0.0350
b_1	0.118	0.00616	19.14	<0.001	0.0104
b_2	0.219	0.0212	10.34	<0.001	0.0339
b_3	0.00101	0.0000569	17.76	<0.001	0.0000860

The standard error for bootstrap sample with B = 1000.

Phosphorus Sorption Estimated by Sorption Curves

Examples of P sorption by aggregates are shown in Figure 4.13. Coefficients of determination (r^2) and the standard errors (Se) for the three sorption equations are presented in Table 4.3, for P sorption by aggregates after 6 days equilibrium. The best fitting equation for all aggregate fractions was the Freundlich equation, represented by the lowest Se value (Figure 4.13). This may be because the Freundlich equation, although originally empirical, implies that the affinity for P sorption decreases exponentially with increasing saturation in the surface, which is probably closer approximation of reality than the assumption of constant binding energy inherent in the

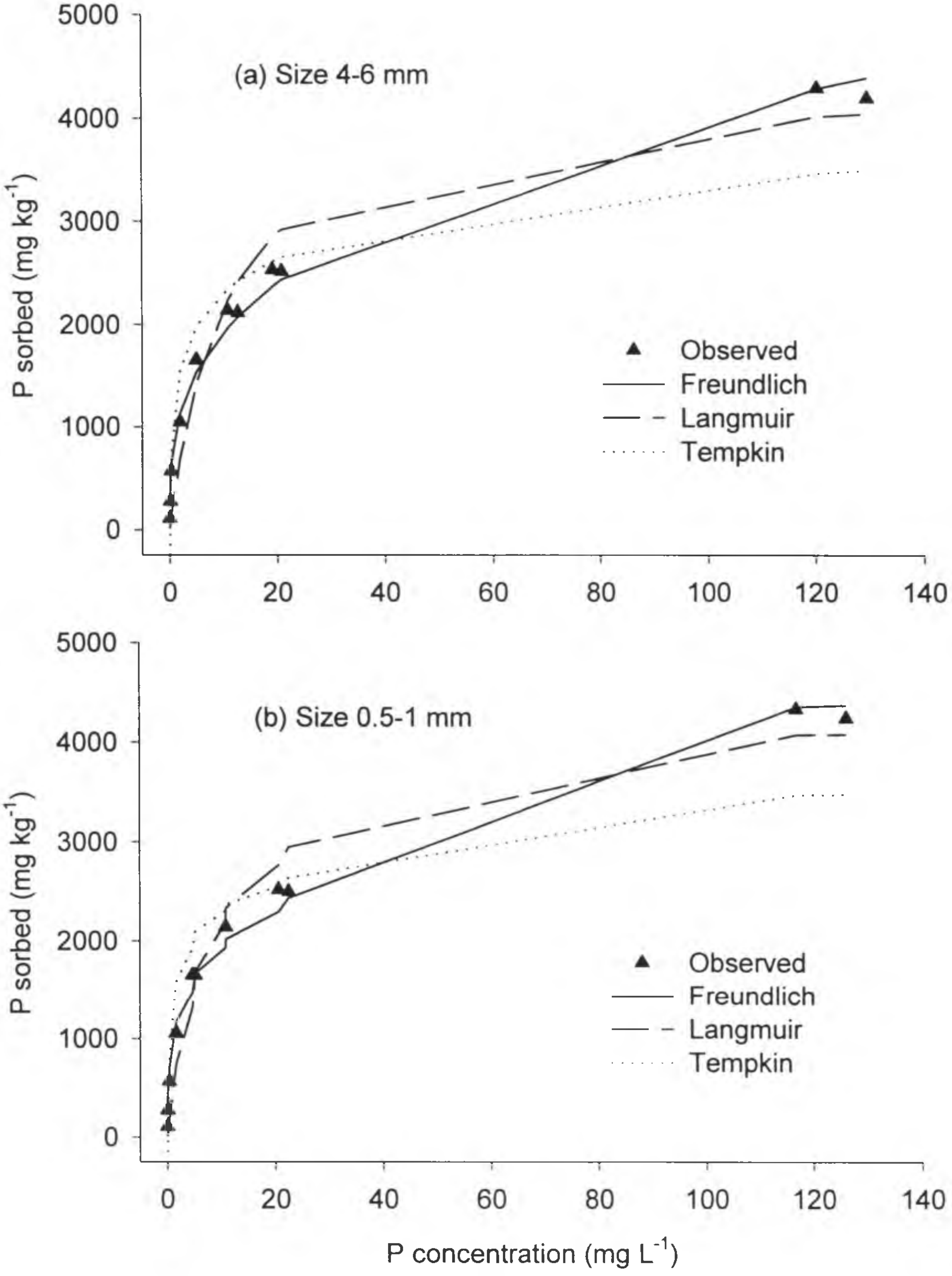

Figure 4.13. Comparisons of adsorption curves for P sorption at 298° K by the Leilehua soil.

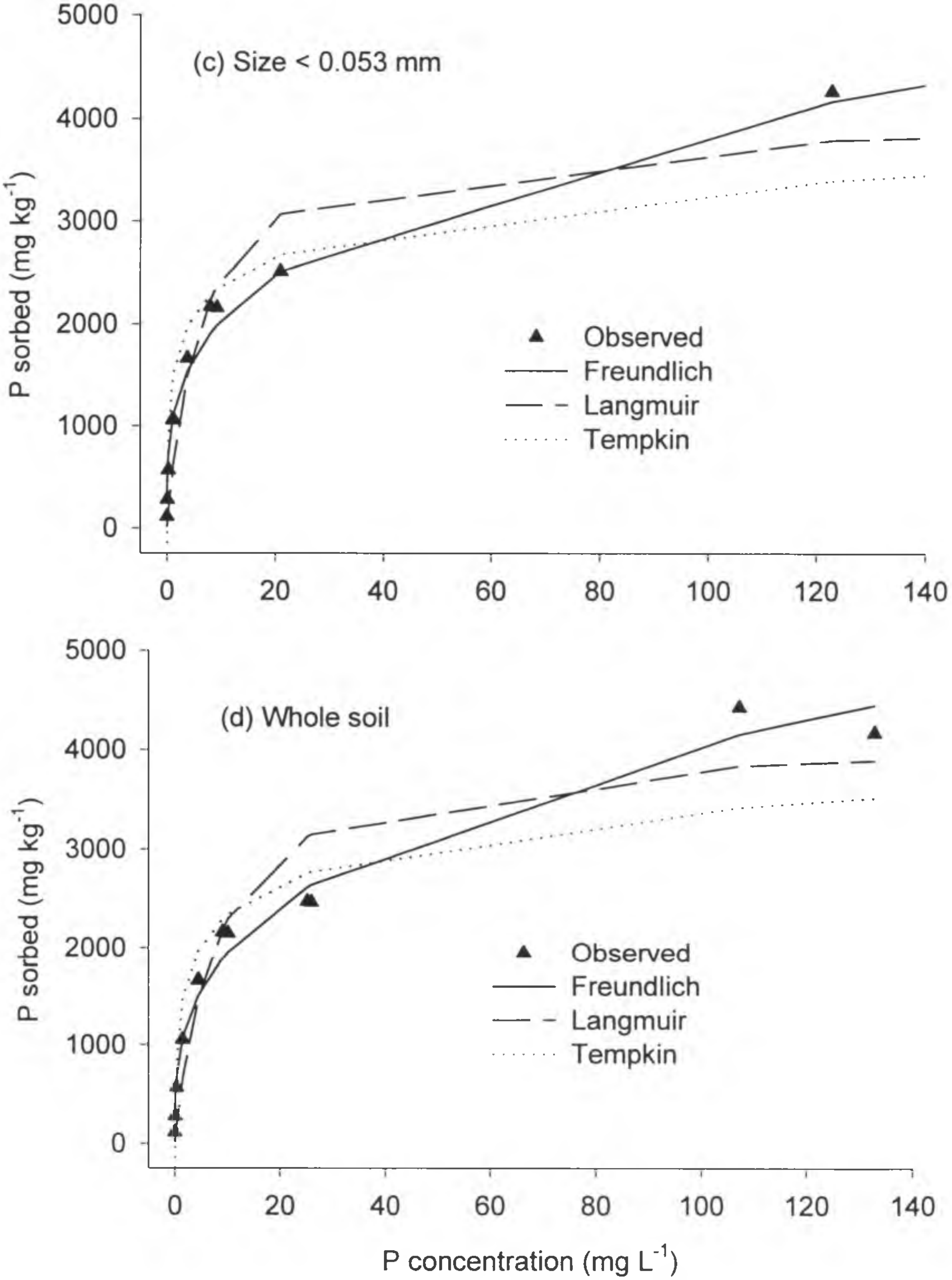

Figure 4.13 (Continued). Comparisons of adsorption curves for P sorption at 298° K for the Leilehua soil.

Table 4.3. Coefficients of determination (r^2) and standard errors (Se), and estimated P sorption at 0.2 mg P L^{-1} ($PS_{0.2}$) of the three sorption equations for P sorption in the Leilehua soil and aggregates.

Size	Model	r^2 †	Se	$PS_{0.2}$
4-6	Freundlich	0.990	131	541
4-6	Langmuir	0.961	310	83
4-6	Tempkin	0.900	437	479
2-4	Freundlich	0.990	142	548
2-4	Langmuir	0.961	315	83
2-4	Tempkin	0.896	454	520
1-2	Freundlich	0.996	133	557
1-2	Langmuir	0.945	356	91
1-2	Tempkin	0.899	441	547
0.5-1	Freundlich	0.992	134	549
0.5-1	Langmuir	0.953	336	86
0.5-1	Tempkin	0.888	458	563
0.25-0.5	Freundlich	0.987	152	555
0.25-0.5	Langmuir	0.968	288	87
0.25-0.5	Tempkin	0.889	461	524
0.125-0.25	Freundlich	0.982	184	651
0.125-0.25	Langmuir	0.924	413	135
0.125-0.25	Tempkin	0.935	365	615
0.053-0.125	Freundlich	0.984	175	670
0.053-0.125	Langmuir	0.930	400	143
0.053-0.125	Tempkin	0.927	381	677
<0.053	Freundlich	0.987	140	661
<0.053	Langmuir	0.939	383	122
<0.053	Tempkin	0.899	454	774
whole	Freundlich	0.982	184	554
whole	Langmuir	0.930	379	99
whole	Tempkin	0.891	446	541

† All r^2 are significant at $p < 0.01$.

Langmuir equation (Sposito, 1984). The Tempkin equation did not adequately predict the highest values of P sorption, probably due to invalid assumptions of the equation (Barrow, 1978; Hayward and Trapnell, 1964). The Langmuir equation underestimated P sorption at lower P concentrations and overestimated P sorption at higher concentrations (Figure 4.13).

Phosphorus sorption at equilibrium concentration of 0.2 mg P L^{-1} ($PS_{0.2}$) was estimated from the fitted equations. The ranges of $PS_{0.2}$ were 80 - 150, 540 - 670, 475 - 775 mg P kg^{-1}, for the Langmuir, Freundlich, and Tempkin equations, respectively. On the other hand, a range of 380 - 600 mg P kg^{-1} soil at 0.2 mg P L^{-1} in solution was observed in the experiment. The values of $PS_{0.2}$ predicted using the Freundlich equation were closest to observed values.

The sorption curves generally shift to the left as aggregate size decreased from 4-6 mm to < 0.053 mm (Figure 4.14). This indicates an increase in P sorption with decreased aggregate size. The correspondence between sorption rate and decreased aggregate size, however, was not perfect: from left to right, the curves were associated with aggregate sizes of 0.053-0.125, 0.125-0.25, 0-0.053, whole soil, 0.25-0.5 or 0.5-1, and 1-2 or 2-4 or 4-6 mm. These results were not completely consistent with previous findings that suggest an increase in P sorption with decreased aggregate size (Gunary et al, 1964; Willet et al., 1988; and Linquist et al., 1997). Rough outer surfaces and the existence of cracks or relatively large intra-aggregate pores in aggregates may be responsible for the small difference in initial P sorption among the aggregates with sizes

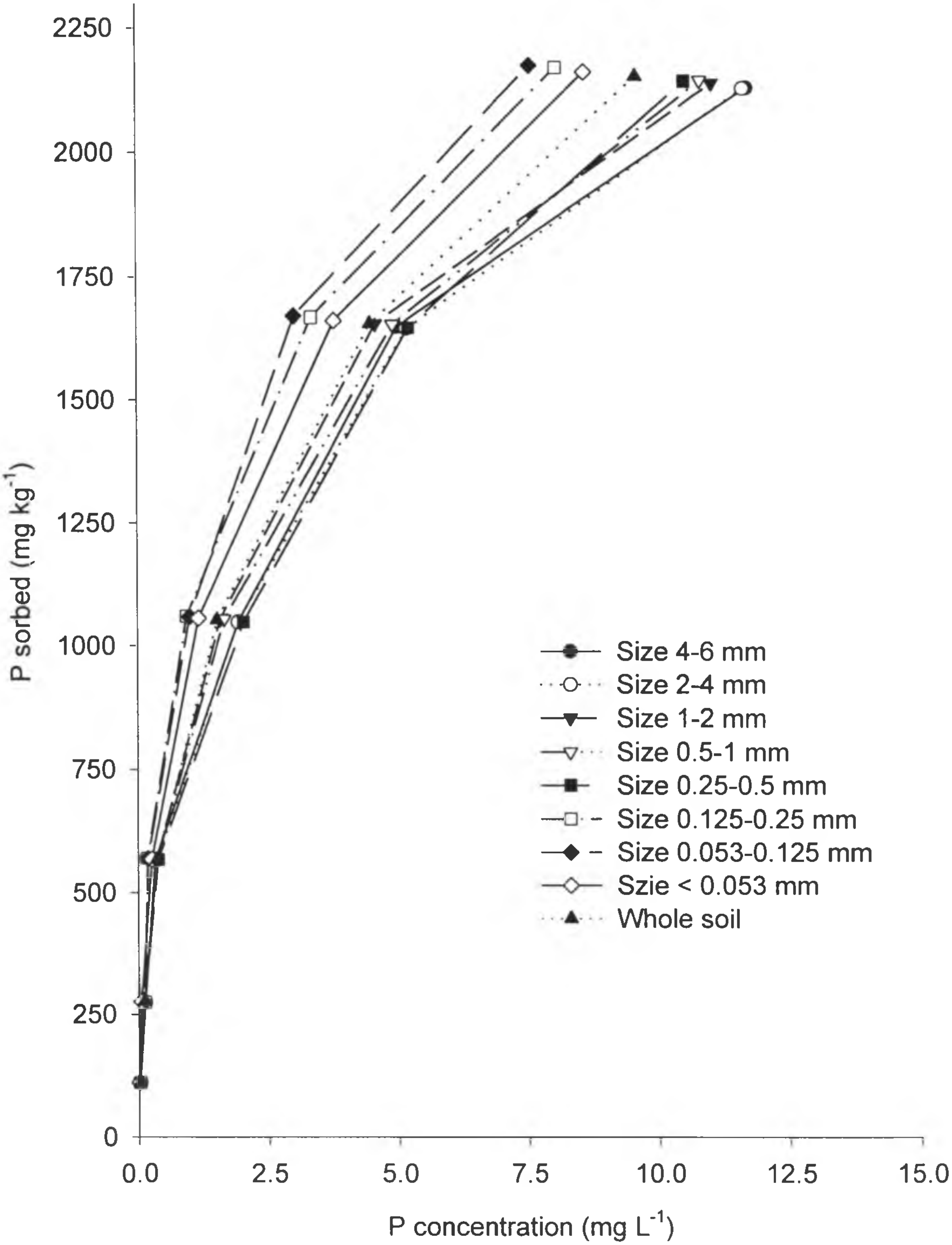

Figure 4.14. Phosphate sorption curves by aggregate fractions and whole soil of the Leilehua soil at 298° K (6 days). Soil:solution = 1:10.

of 1-2 or 2-4 or 4-6 mm. Such effects on surface area due to rough outer surfaces and cracks, however, probably are small relative to the large estimated differences in surface area of the smaller size fractions. The surface areas of the aggregate fractions of 0-0.053, 0.053-0.125 and 0.125-0.25 mm were estimated at 180, 64, and 31 m^2 kg^{-1}, respectively, calculated on the basis of the volume-weighted mean diameter. Effects of surface roughness, therefore, may not explain why P sorption by the 0-0.053 mm aggregates was less than P sorption by the aggregates of 0.053-0.125, and 0.125-0.25 mm. The internal surface area of aggregates may need be considered, probably because of P diffusion into aggregates in well-stirred solutions.

Phosphorus sorption ($PS_{0\,2}$) and P buffer coefficient estimate (the first derivative) at 0.2 mg P L^{-1} ($PBC_{0\,2}$) estimated from the Freundlich equation were not related to effective mass, aggregate diameter, and surface area. This poor relationship suggests that both internal and outer surface area of aggregates should be considered as factors to influence P sorption.

Phosphorus Sorption Kinetics

Examples of P sorption kinetics by aggregates of differing size are shown in Figure 4.15. Coefficients of determination and the standard errors for four kinetic equations are presented in Table 4.4 for P sorption by aggregate fractions. The best fitting equation, the Elovich equation, among the candidate models is represented by the highest r^2 and lowest standard error. The other equations had lower r^2 and higher

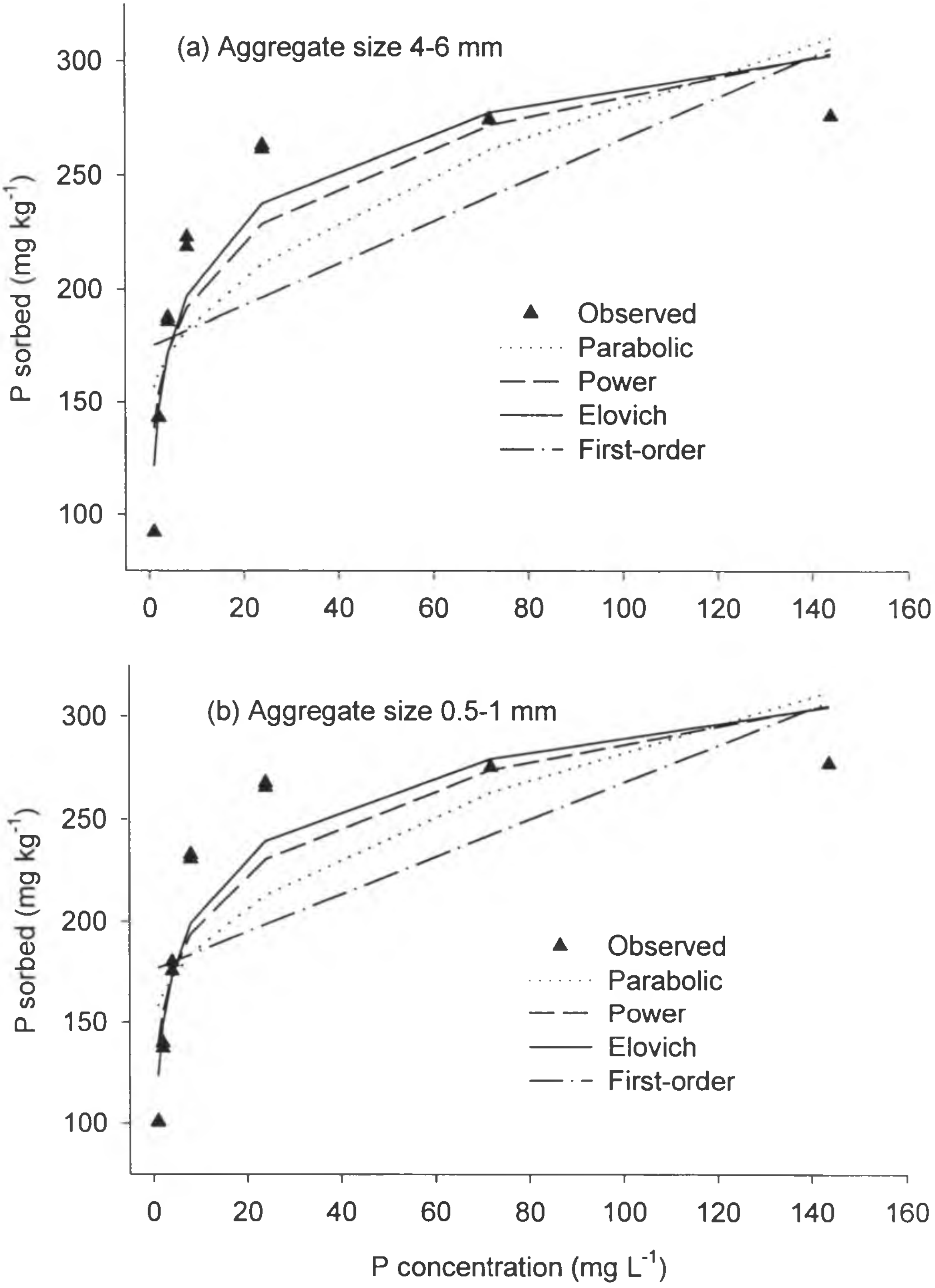

Figure 4.15. Comparisons of various kinetic models for P sorption at 298° K for the Leilehua soil.

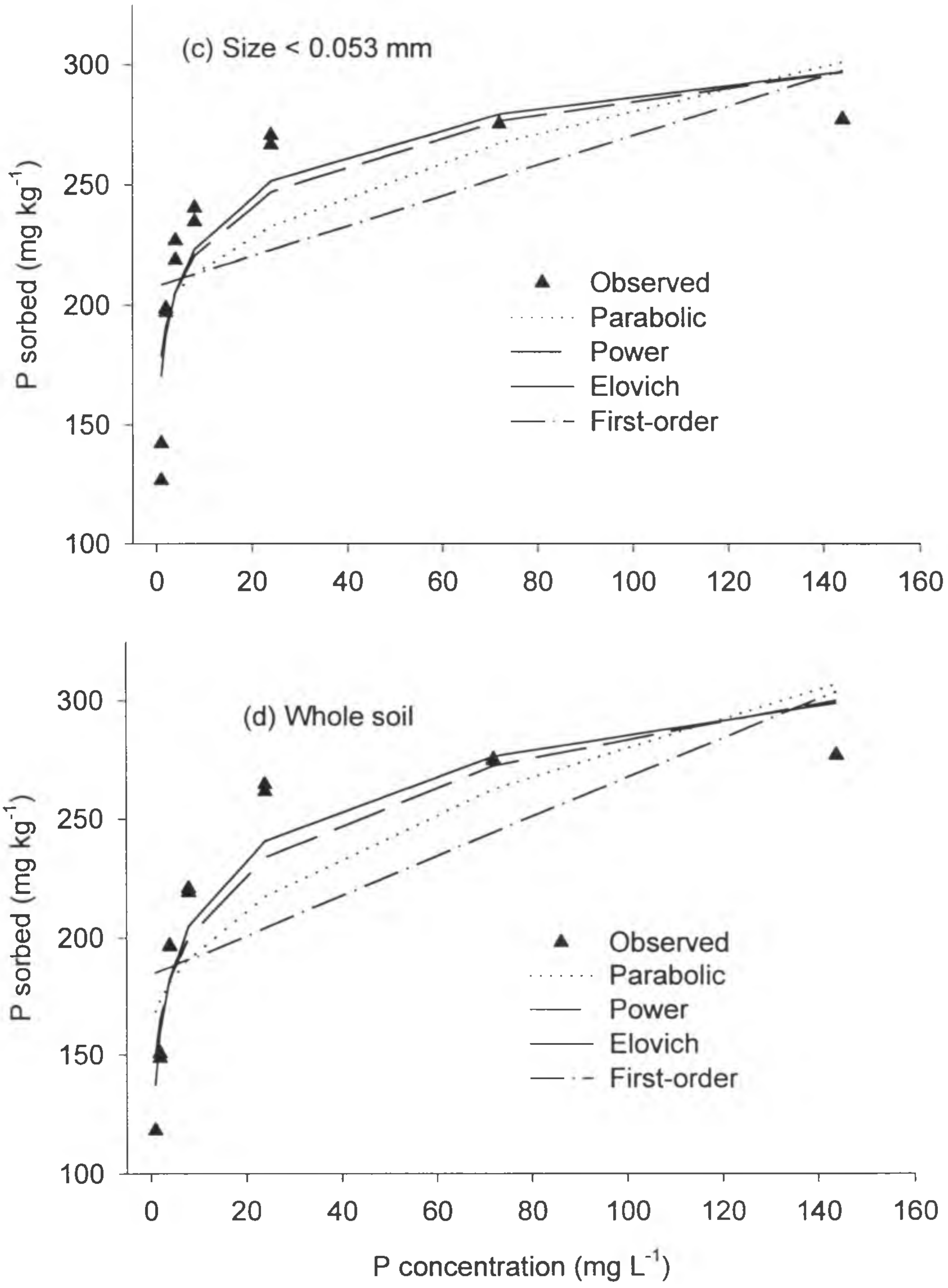

Figure 4.15 (Continued). Comparisons of various kinetic models for P sorption at 298° K for the Leilehua soil.

Table 4.4. Coefficients of determination (r^2) and standard error (Se) of the four kinetic equations for P sorption in the Leilehua soil and aggregates.

Size	Parabolic equation[†]		Power equation[†]		Elovich equation[†]		First-order equation[†]	
(mm)	r^2[‡]	Se	r^2	Se	r^2	Se	r^2	Se
4-6	0.661	41	0.829	28	0.901	21	0.473	50
2-4	0.690	40	0.849	27	0.920	20	0.499	49
1-2	0.689	40	0.848	27	0.918	20	0.498	49
0.5-1	0.654	42	0.823	29	0.895	22	0.463	50
0.25-0.5	0.651	36	0.834	24	0.894	19	0.461	43
0.125-0.25	0.631	31	0.827	20	0.875	17	0.443	37
0.053-0.125	0.623	30	0.822	20	0.870	17	0438	37
<0.053	0.588	33	0.784	23	0.834	20	0.414*	38
whole	0.694	35	0.863	22	0.921	17	0.503	43

[†] Parabolic equation: $Q = a + k\,t^{1/2}$;
Power equation: $Q = k\,t^{v}$;
Elovich equation: $a + (1/b)\ln(t)$;
First-order equation: $Q/Qm = 1 - \alpha \exp(-\beta t)$.

[‡] Significance of r^2 is $p < 0.01$, unless otherwise stated as * ($p < 0.05$).

standard error values. Figure 4.15 shows the data fit to the four models for selected aggregate fractions and whole soil. It is evident that deviations of predicted P sorption from observed values for all the four models were great, suggesting limitations of the empirical kinetic equations. Some mechanistic models, based on solution P diffusion into aggregates with P sorption, may be helpful for describing P sorption kinetics.

As shown in the P sorption experiment, the kinetic curves shift to the left when aggregate size decrease from 4-6 mm to 0-0.053 mm (Figure 4.16). The sorption curve of the whole soil was close to the aggregate fractions of 0.25-0.5 and 0.5-1 mm.

Phosphorus Diffusion model

In general, change in P sorption with P concentration is nonlinear. The linear relationships between P sorbed by aggregates and P concentration in solution, however, were evident in a range of 0 - 10 mg P L^{-1} (Figure 4.17). Thus, a simple linear model was used to estimate β and the values of β are shown in Table 4.5. The values of β increased as aggregate size decreased from 4-6 mm to 0.125-0.25 mm, then decreased as aggregate size decreased from 0.125-0.25 mm to <0.053 mm. The correlations between β and aggregate diameter, area, effective mass were generally poor (data not shown).

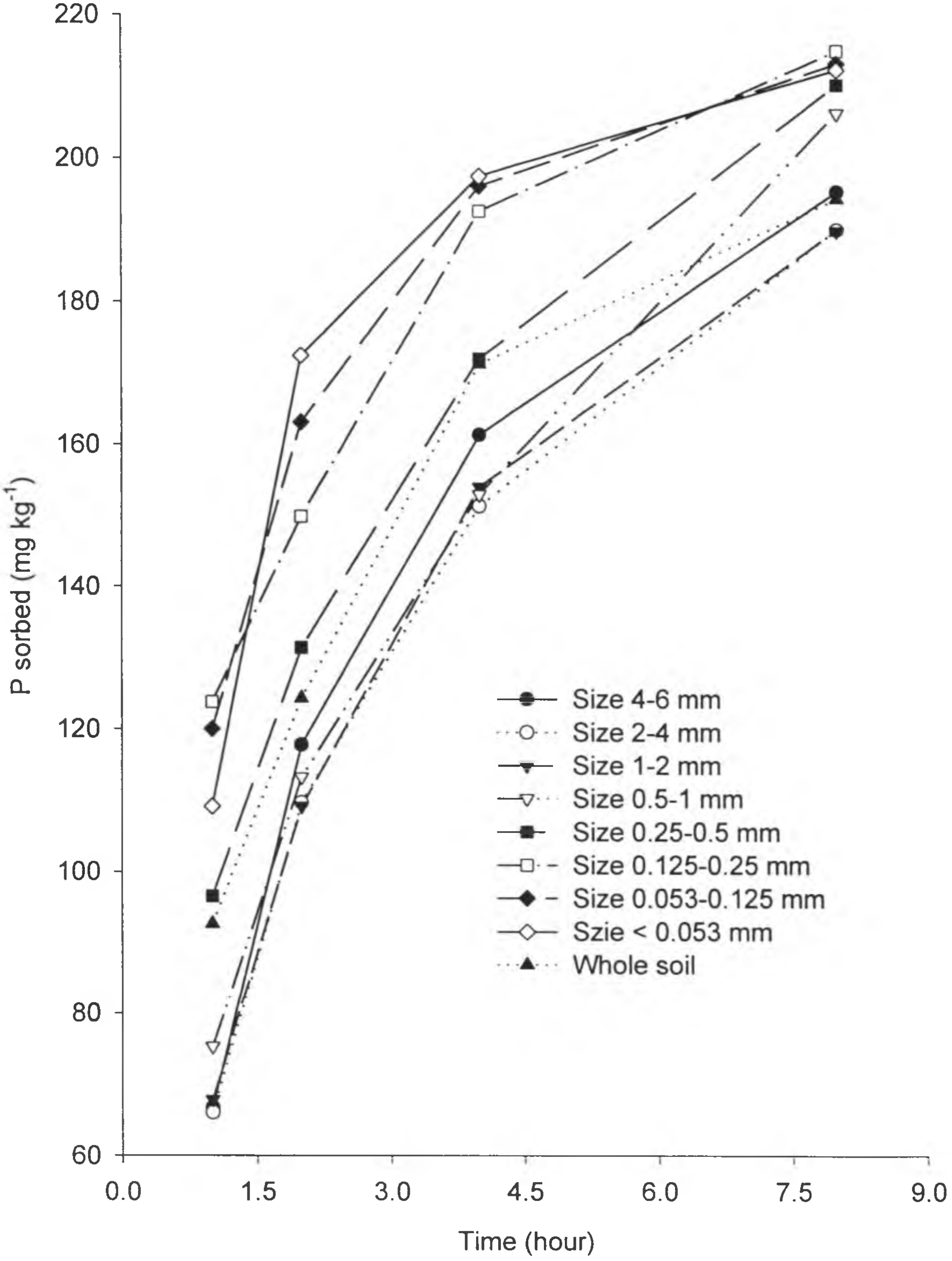

Figure 4.16. Phosphorus sorption by aggregate fractions and the whole soil of the Leilehua soil as a function of time at 298° K. Soil:solution ratio=1:10.

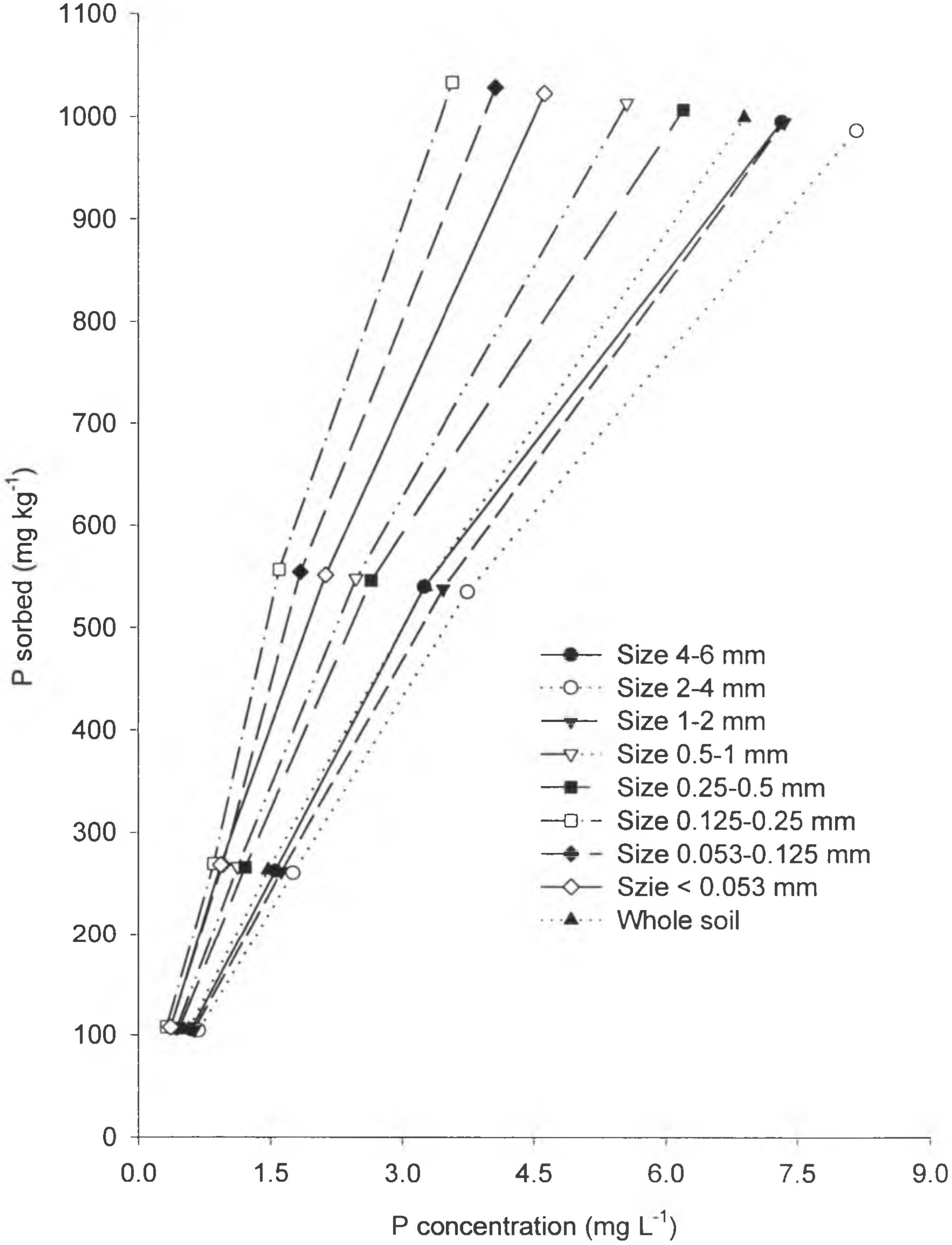

Figure 4.17. Phosphorus sorption curves by aggregate fractions and whole soil of the Leilehua soil at 298° K(1 day). Soil:solution = 1:10.

Table 4.5. Phosphorus buffer coefficient (β), and effective diffusion coefficient (D_e)[†] of various aggregate fractions and whole soil for the Leilehua soil.

Size (mm)	β	D_e (m^2 s^{-1})
4 - 6	130	3.00×10^{-15}
2 - 4	116	3.36×10^{-15}
1 -2	131	2.99×10^{-15}
0.5 - 1	173	2.26×10^{-15}
0.25 - 0.5	153	2.55×10^{-15}
0.125 - 0.25	282	1.39×10^{-15}
0.053 - 0.125	247	1.59×10^{-15}
< 0.053	211	1.86×10^{-15}
whole	139	2.81×10^{-15}

[†] $De = D_L f/(1+\rho_b\beta/\theta)$, where $D_L = 9 \times 10^{-10}$ m2 s^{-1}, $\rho_b = 1.3$, $\theta = 0.567$ (assuming particle density equals 3).

The change in effective diffusion coefficient with aggregate size was the same as the change in β because impedance factor f was fixed at $f = 0.001$. This assumption may not be realistic. Even if the porosity of intra-aggregate pores is roughly the same for differing aggregate fractions (see Chapter 2), the connections between the intra-aggregate pores may be different, dependent on an individual aggregate fraction. Nevertheless, incorporation of these parameters into conceptual models such as equation (4.11) may be useful for understanding the effects of β and f on P sorption.

If P sorption in aggregates obeys diffusion kinetics, P will probably be first sorbed at the outer surface of aggregates. Then P may diffuse from the outside of the aggregate into the inside, where P reacts with the sorption sites within aggregates. The slow decline in solution P with time is consistent with P diffusing into the aggregates. Analysis of kinetic data may, however, not give precise information concerning the diffusion processes that are rate determining. Various processes, all of which may reduce solution P or extractable P, can occur simultaneously and give results that are indistinguishable from one another.

CONCLUSIONS

The effects of aggregate size on P status in the Leilehua soil from Hawaii were assessed with P sorption, 0.5 *M* $NaHCO_3$ extractable P (available P), and 0.001 *M* $CaCl_2$ extractable P (soil solution P). After P was added to a mixture of differing aggregate size fractions, P sorption and extractable P in subsequently separated aggregates decreased as aggregate size increased from < 0.5 to 4 - 6 mm. The decrease in extractable P with increasing aggregate size, however, became small with prolonged incubation time.

The decline in extractable P with time was much greater than the decline in solution P. The heterogeneity of extractable P among aggregates for highly aggregated soils remained even after several years (Chapter 3). Continuous P reactions with unoccupied P sorption sites in soils is, therefore, probably another reason for declines of fertilizer effectiveness with time.

By contrast, P sorption decreased, 0.001 *M* $CaCl_2$ extractable P increased as aggregate size increased after P was added to separated aggregate fractions. The change in 0.5 *M* $NaHCO_3$ extractable P with aggregate size was dependent on the level of P added. At 0-200 mg P kg^{-1}, extractable P increased with increased aggregate size while extractable P was greater at both small and large aggregate sizes when 200 - 800 mg P kg^{-1} was added.

Phosphorus sorption curves and kinetics for differing aggregate fractions were described by the Freundlich equation and the Elovich equation, respectively. Higher deviations from observed data using the empirical equations for P sorption kinetics were evident. Mechanistic models such as the P diffusion model may be needed. The difficulty in estimating P diffusion coefficients in intra-aggregate pores, however, prevents the application of the diffusion model in P sorption kinetics.

The reduced P sorption and increased solution P by increased aggregate size suggest that grinding and shaking soil sample used in P analysis may over-estimated P requirements by under-estimating soil P availability because diffusion-limited P sorption sites are exposed to increase P sorption.

CHAPTER 5

EFFECT OF SOIL AGGREGATE SIZE ON PHOSPHORUS DESORPTION FROM P-ADDED SOILS AND PHOSPHORUS ABSORPTION

ABSTRACT

Knowledge of the degree of reversibility of sorbed P in soils is of great agronomic significance because P desorption is a limited factor for P uptake by crops. The reduced soil P sorption with increasing aggregate size suggest that soil aggregation may affect P release from aggregates. The objective of this study was to determine to the effect of aggregate size on P bioavailability of three highly weathered soils with a column-leaching study and a pot experiment. Phosphorus desorption from subsequently separated small aggregates was greater than from large aggregates when P had been added to the whole soils (the Kappa and Leilehua soil) and a mixture of differing-size aggregates (the Leilehua soil). When P was added to separated aggregates, however, P desorption was initially greater from large aggregates (4-6 mm) than from small aggregates (< 0.5 mm). The total P in soybean and lettuce shoots, and the root dry weights grown in the large aggregates (2-6 mm) were higher than in the small aggregates (<0.5 mm) after P was added to the separated aggregate fractions. The increased P uptake by crops with increasing aggregate size was due to increased P desorption from aggregates through reduced P sorption. Soil managements that favor soil aggregation would increase P availability and should be considered in P management decisions.

INTRODUCTION

Assessment of phosphorus (P) bioavailability in soils is important to consider from perspectives of sustainable agriculture and protecting our environment. Although influences of soil chemical properties on P release from soils and uptake by plants are well documented, we still suffer from imprecision in P diagnosis and recommendation. Cassman et al. (1993) found that application 100 kg P ha^{-1} to the Haiku soil produced a maximum yield, although the recommended P application rate, based on the Fox and Kamprath method, was more than 500 kg P ha^{-1} in the earlier experiment (Cassman et al., 1981). One possible solution to the imprecision is to try to better understand the processes controlling P sorption reaction and desorption from soils. Few studies, however, have examined the roles of soil physical properties in P desorption and uptake. Studies of nutrient uptake with aggregates of varying size show that P uptake from small aggregates was greater than that from large aggregates (Wiersum, 1962; Cornforth, 1968; Misra et al., 1988a). On the other hand, freshly applied P probably penetrates a thin layer around soil aggregates (Gunary et al., 1964; Linquist et al., 1997), suggesting the possibility that soil aggregation may reduce P fixation and increase P availability.

In well-aggregated soils, major solute transport often occurs in the inter-aggregate pore system. In this case, the accessibility of the solid surface by the liquid phase is reduced considerably by aggregate formation. Consequently, actual nutrient accessibility and uptake by plant roots would be expected to differ because of aggregation.

Soil P release is a key feature in P supply to plants and P discharge into watersheds. A study of P desorption would, therefore, appear to be more pertinent than P sorption when evaluating the plant-available P and the P buffering properties of soils -- an observation noted many years ago by Fox and Kamprath (1970). Several experimental techniques have been used to investigate P desorption behavior. These include extraction of soil P with P-free solution, addition of materials with high capacities to bind P in order to deplete P in soils, and leaching of soil columns with P-free solutions. The method of soil column leaching was used in this experiment because it prevented breakup of soil aggregates resulting from vigorous shaking employed by the other methods. Soil column leaching also provided for removal of desorbed P with time, which simulated nutrient removal by plant uptake more closely than batch equilibration.

Objectives of this study were to: 1) investigate the effect of aggregate size on P bioavailability as measured by extractable P and P desorption from different soils and aggregates of varying size; 2) test the hypothesis that aggregation may increase P uptake by plants, through decreasing P sorption, using soybean and lettuce in the greenhouse.

MATERIALS AND METHODS

Soils

Two Oxisols (Kapaa and Wahiawa series) and an Ultisol (Leilehua series) from Hawaii were selected for this study. The preparations of the soils were the same as

Chapter 2 and 3. The classifications of the soils are shown in Table 2.1. Selected properties of the soils are presented in Table 5.1.

Table 5.1. Selected properties of the soils.

Soil series	pH	P applied	Olsen P	GMD[†]
Kapaa	5.5	1.6 mg P L^{-1}[‡]	204	1.253
Wahiawa	5.9	1.6 mg P L^{-1}[‡]	283	0.655
Leilehua	4.5	800 mg P kg^{-1}	198	0.988

[†] GMD: geometric mean diameter (mm).

[‡] P rate was based on the P sorption isotherm curve (Fox and Kamprath, 1970).

For the Wahiawa and Kapaa soils, eight aggregate size fractions were obtained using a dry-sieving method. The aggregate sizes were < 0.053, 0.053-0.125, 0.125-0.25, 0.25-0.5, 0.5-1, 1-2, 2-4, and 4-6 mm. For the Leilehua soil, a mixture of equal amounts of varying-size aggregates (< 0.5, 0.5-1, 1-2, 2-4, 4-6 mm) was enriched with P (800 mg kg^{-1}), incubated for 180 days (Experiment I in Chapter 4), and then separated into the original size aggregates. The 0.5 *M* $NaHCO_3$ extractable P in different aggregate fractions and whole soils was determined (Olsen et al., 1954). The colormetric method for determining P in solution uses ammonium molybdate reagent with ascorbic acid according to the Murphy and Riley (1962) and Watanabe and Olsen (1965) procedures.

Phosphorus Desorption

Soil column leaching was used to determine the influence of aggregate size on P desorption. The aggregate fractions used in the column leaching were < 0.5, 1-2, 4-6 mm, and whole soil (< 2 mm) for the Leilehua soil from *Experiment I* (Chapter 4) with an incubation of 180 days and 800 mg P kg^{-1}; 0.053-0.125, 0.5-1, 4-6 mm, and whole soil (< 2 mm) for the Wahiawa soil; and 0.125-0.25, 1-2, 4-6 mm, and whole soil (< 2 mm) for the Kapaa soil. Ten grams of each sample were packed into a syringe (50 cc) with acid-washed quartz sand at both ends. The soil columns were saturated with 0.001 *M* $CaCl_2$ from the bottom. Constant solution flux of 0.001 *M* $CaCl_2$ through the vertical column was maintained with a peristaltic tubing pump. The flux was maintained at 2.3 x 10^{-5} m s^{-1}. This flux was below the saturated hydraulic conductivity of the column for all soil samples because no water layer at the top of the column was observed. The leachate was collected at an interval of 25 minutes for 2 to 6 weeks and solution P was determined in all fractions collected. The cumulative desorbed P was then calculated from the P concentration and volume of the effluent. The experiment was replicated with two times.

In order to separate the effects of aggregate size and the initial extractable P level on P desorption, P was individually applied at a rate of 800 mg P kg^{-1} to separated aggregates of the Leilehua soil. Aggregate sizes were < 0.5, 0.5-1, 2-4, 4-6 mm; the size fractions contained similar levels of extractable P prior to P addition. Samples were incubated for 28 days as described in Chapter 4. Phosphate desorption from these individual aggregate fractions was then determined using column leaching.

At the end 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 over 92% except for the aggregate size 4 - 6 mm of the Wahiawa soil. The 4-6 mm aggregate of the Wahiawa soil broke into aggregates less than 2 mm in size after column leaching.

Kinetic Curves and P Desorption Rate

Investigation of the kinetics of P desorption with pore volume should expand our understanding of nutrient release processes. The information, such as rate of P release, derived from the kinetic equation may be dependent on soil characteristics and be related to plant growth and P uptake. Kinetic curves were obtained by plotting the amount of cumulative desorbed P against pore volumes rather than time. Several kinetic equations were evaluated in their ability to fit P desorption data using graphical, linear, and nonlinear regression procedures with S-PLUS version 3.3 (Statistical Science, 1995). The parabolic diffusion, power function, simple Elovich, and an expanded Elovich equation were considered (Table 5.2). The descriptions of soil P desorption kinetics with these equations are well documented (Chien and Clayton, 1980; Kuo and Lotse, 1974; Polyzopoulos et al. 1986; Raven and Hossner, 1994; Vig and Dev, 1979). The fit of these equations was evaluated with both the coefficient of determination (r^2) and standard error (Se). The first- and second-order equations were not considered because preliminary graphical tests (not shown) indicated that these equations did not adequately describe the P desorption data.

Table 5.2. Equations that were evaluated for their ability to describe the P desorption kinetic data.

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); PV = pore volume; a, b, c = constants.

The intent of this study was to investigate effects of aggregate size on the rate of P release from soils. The change in P desorption with pore volume (soil P desorption rate) was defined as the slope of the kinetic curve (the first derivative) at 10 pore volumes, calculated from the best fitting equation, and related to aggregate diameter. This could be the initial P desorption rate. The final P desorption rate is obviously experiment-specific, and is not discussed in this paper.

Pot Experiment

A pot experiment was conducted in the greenhouse to determine the effect of aggregate size on P uptake by lettuce (*Lactuca sativa*) and soybean (*Glycine max*) in the Leilehua soil. The P deficient Leilehua soil was first separated into aggregates with sizes of <0.5, 0.5-2, and 2-6 mm. The initial 0.5 *M* $NaHCO_3$ extractable P in aggregate fractions ranged from 1-1.8 mg P kg^{-1}. Each fraction of aggregates, and the whole soil was equilibrated with 0, 62.5, 125, 250, and 500 mg P kg^{-1} soil (P applied as monobasic calcium phosphate) four weeks before planting. The soil samples were mixed with vermiculite (1:1 by volume) to minimize the differences in water holding capacity due to differing sized aggregates. The seeds of lettuce and soybean were directly planted in the pot. The seedlings were thinned to five per pot. The lettuce and soybean plants were harvested 30 and 32 days after planting, respectively. 0.5 *M* $NaHCO_3$ extractable P in aggregates was measured before planting and after harvest.

All roots were separated from soils, and were cleaned with water. Plant tops (shoots) and roots were oven-dried at 70° C, and the dry weights were recorded. The dry plant tops were ground. Duplicate samples of 0.2000 g were dry-ashed in a muffle furnace at 500 ° C for four hours. The ash was dissolved in 0.1 *M* HCL solution. The P concentration in ashed samples were determined by the phosphomolybdate method (Murphy and Riley, 1962).

The experimental design was a randomized block for each crop, with five P rates (0, 62.5, 125, 250, 500 mg P kg^{-1} soil), four aggregate sizes (2 - 6, 0.5 - 2, < 0.5 mm, and whole soil passing a 2 mm sieve), and three replicates (as blocks). Phosphorus rate and aggregate size were treated as fixed factors because of intrinsic interest in them. An ANOVA table for P uptake and dry weight of roots was constructed. The adequacy of the model being employed was evaluated with a set of plots including a histogram of residuals, normal quantile-quantile plot (qqplot) of residuals, and scatter plot of residuals versus fitted values. Diagnostic plots indicated no outliers or lack of homogeneity in error variances for the soybean data sets. However, there were non-constant error variances and outliers for the lettuce data. The logarithmic transformation of the total P in shoots and dry weight of roots substantially reduced the lack of fit at large values, as expected. No attempt was made to remove an outlier in the residual plots.

The least significant difference (LSD) at the 95% significance level was used for comparing a difference between two treatment means.

RESULTS AND DISCUSSION

Phosphorus Desorption

Differences in P desorption among the three soils were much greater than might be expected from 0.5 *M* $NaHCO_3$ extractable P (Figure 5.1). For example, the cumulative desorbed P at 1000 pore volumes was 25, 125, and 275 mg P kg^{-1} for the Leilehua, Kapaa, and Wahiawa soils, respectively, while initial extractable P in the corresponding soils was 198, 204, and 283 mg P kg^{-1}. The P concentration in 0.001 *M* $CaCl_2$ leachate at the beginning of leaching for the Wahiawa soil was above 2 mg P L^{-1}, much higher than P in the leachate for the Leilehua soil, which was less than 0.1 mg PL^{-1} (data not shown). The rate of P desorption, however, decreased as P desorption proceeded for the Wahiawa soil while the rate of P desorption from the Leilehua soil showed little change with increased pore volume (Figure 5.1). Nevertheless, the rate of desorption remained much greater on the Wahiawa soil. The solubility of P compounds

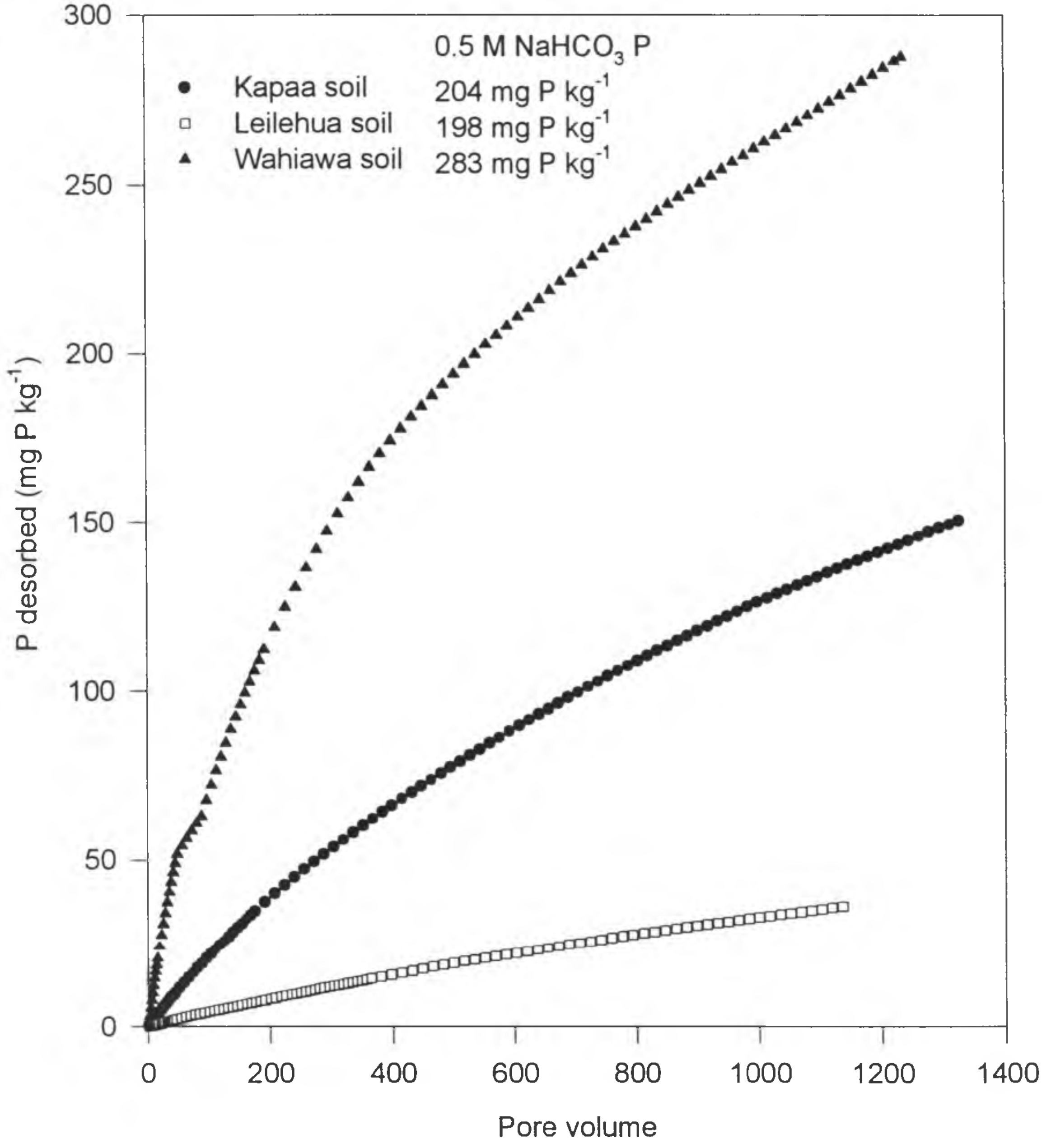

Figure 5.1. Cumulative desorbed P with increasing leaching from three soils, Kapaa, Leilehua, and Wahiawa.

in soils, saturation of P sorption sites, and the added P level probably govern P concentration and release from the soils.

1) Phosphorus Desorption from Aggregates Separated from P-fertilized Soils

The effects of soil aggregate size and extractable P on P desorption are shown in Figures 5.2 through 5.6. After P was added to the whole soil (Wahiawa and Kapaa) or the mixture of differing aggregate fractions (Leilehua), the cumulative P release from subsequently separated small aggregates was greater than from large aggregates (Figure 5.2 through 5.4). The decrease in P desorption with increasing aggregate size may be attributed to the decreasing accessibility of solution to sorption sites within aggregates and the decreasing initial extractable P level as shown in Chapters 3 and 4. The results may explain the observations of Wiersum (1962), Cornforth (1968), and Misra et al. (1988 a) that P uptake from small aggregates was greater than from large aggregates.

The difference in P release from differing aggregate fractions of the Wahiawa soil was small compared to P release from the Kapaa and Leilehua soils (Figure 5.2 *vs.* Figure 5.3 and 5.4. One of the reasons was that extractable P was greater from small aggregate fractions of the Kapaa and Leilehua soils, while there were almost no differences in extractable P for the Wahiawa soil (see Chapter 3 and 4). The other reason may be the breakup of large aggregates during the leaching experiment. Large aggregates (4-6 mm) of the Wahiawa soil broke into smaller aggregates during the leaching. At the end of

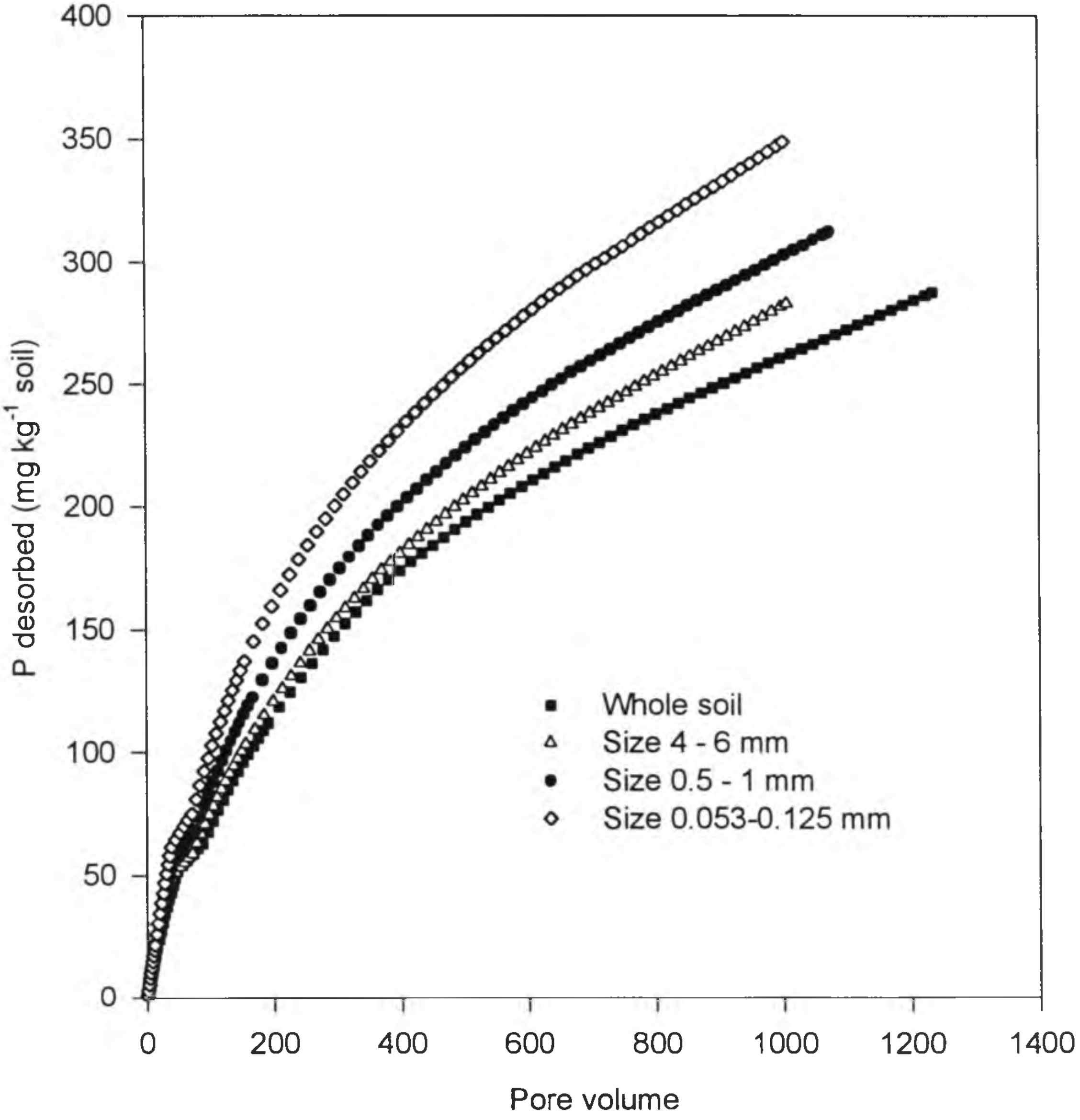

Figure 5.2. Phosphorus desorption from aggregates of varying size after P was applied to the whole soil, Wahiawa soil.

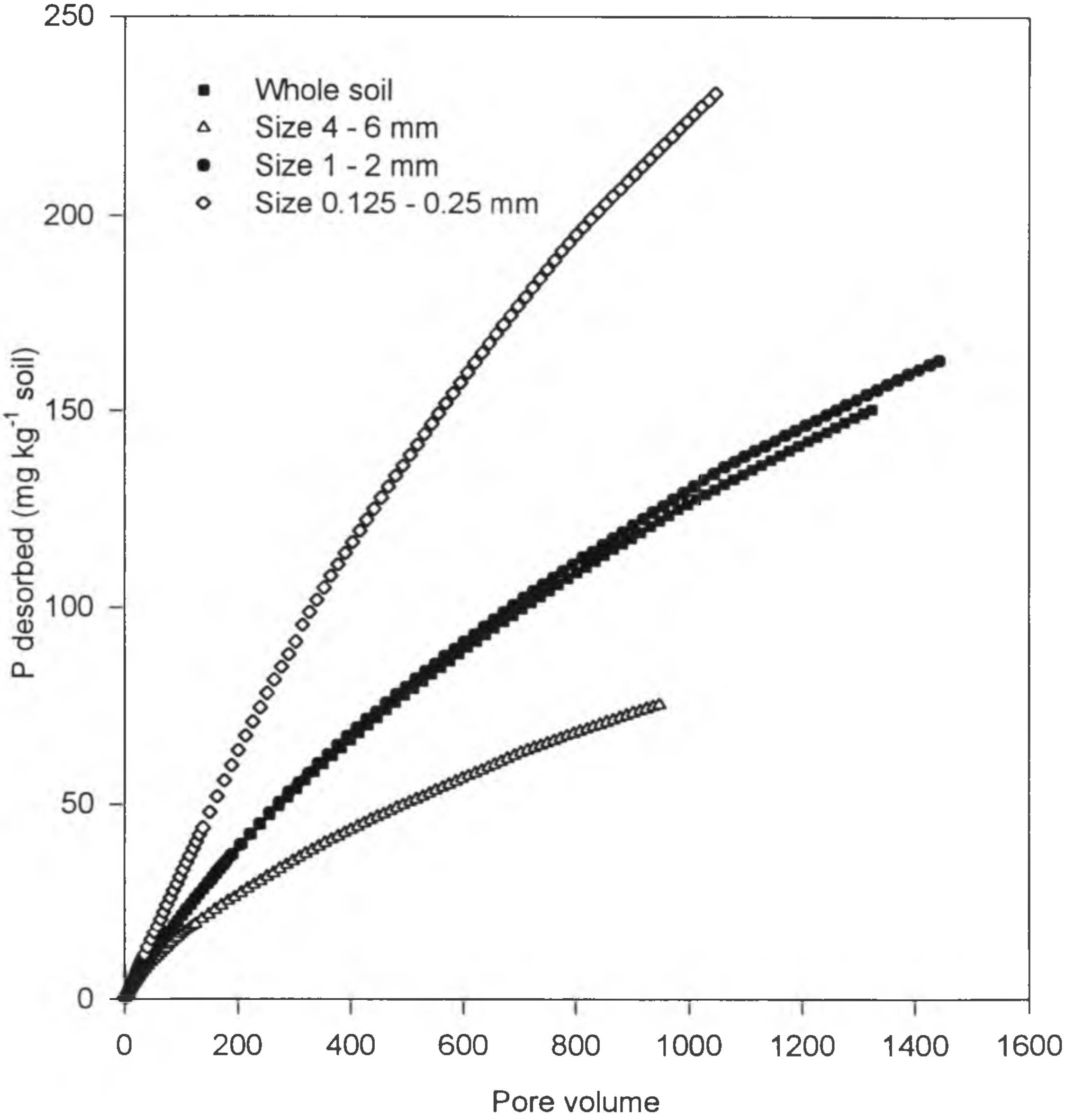

Figure 5.3. Phosphorus desorption from aggregates of varying size after P was applied to the whole soil, Kapaa soil.

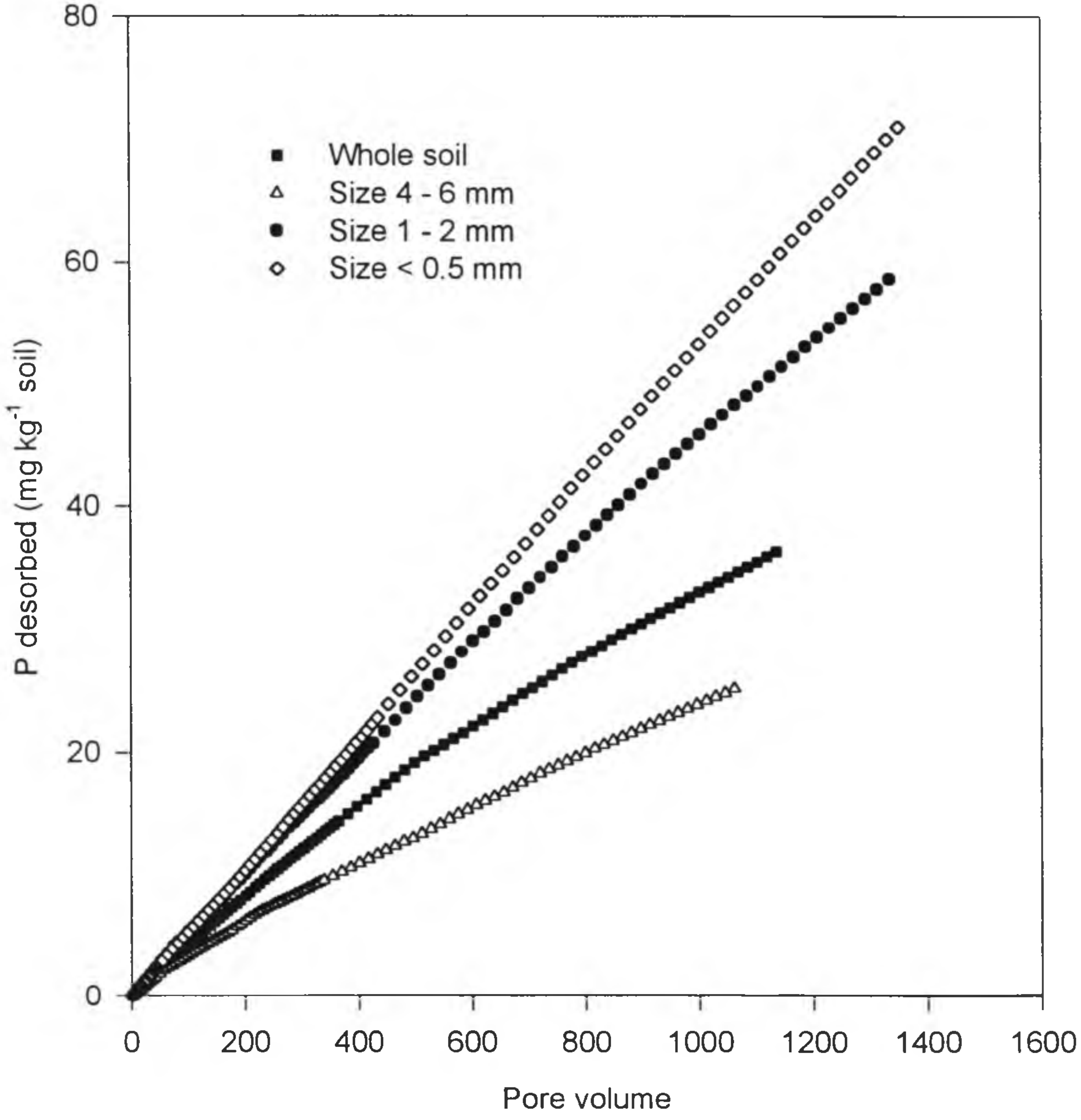

Figure 5.4. Phosphorus desorption from aggregates of varying size. 800 mg P kg^{-1} was added to a mixture of equal amount of differing aggregate fractions, Leilehua soil.

column leaching 19 % of the sample passed a 1 mm sieve and the entire sample passed a 2 mm sieve.

2) Phosphorus Desorption from Separated, P-enriched Aggregates

Phosphorus desorption from large aggregates (4-6 mm) was greater than from small aggregates (< 0.5 mm) at the beginning of leaching after a rate of 800 mg P kg^{-1} was individually added to separated aggregate fractions (Figure 5.5 and 5.6). The decrease in P concentration in leachate from large aggregates, however, was greater than that from small aggregates as additional pore volumes of solution were added. This may demonstrate the lack of accessibility of reactive sites within aggregates by P solution and leachate on P sorption and desorption. The higher initial solution P in leachate from larger aggregates probably indicates less P sorbed. Decreased P sorption with increasing aggregate size is consistent with the finding reported by Gunary et al. (1964), Willet et al. (1988), and Linquist et al. (1997) that initial sorbed P was mainly on the outer surface of aggregates.

3) Accessibility

Three factors probably influence P desorption from aggregates: flow rate (the solution flux of 0.001 M $CaCl_2$ passing through the vertical soil column in this experiment), P sorption, and accessible reactive sites. Increasing aggregate size should decrease P sorption due to decreasing accessibility of reactive sites by P solution and,

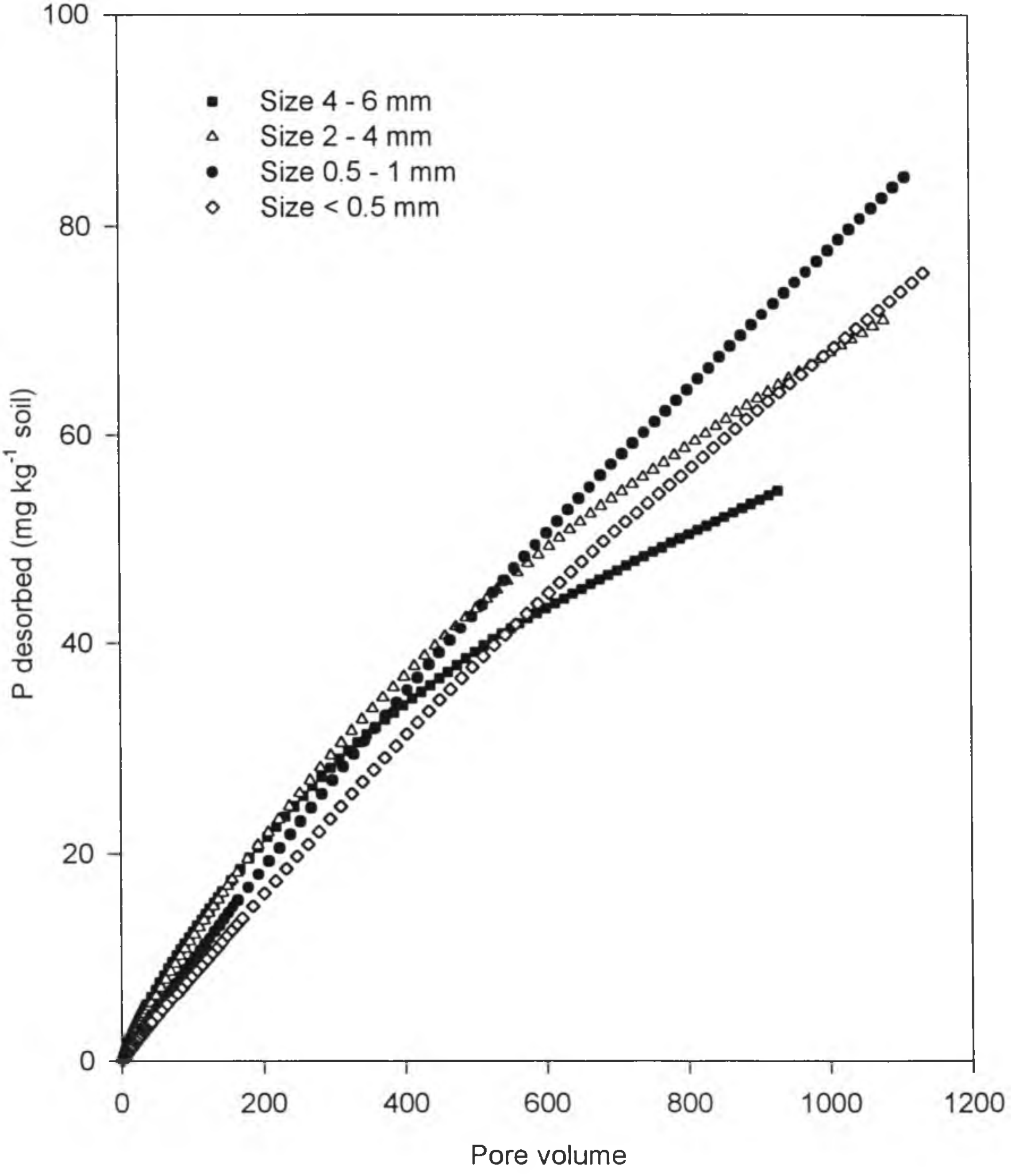

Figure 5.5. Effect of aggregate size on P desorption. 800 mg P kg^{-1} was added to separated aggregates, Leilehua soil.

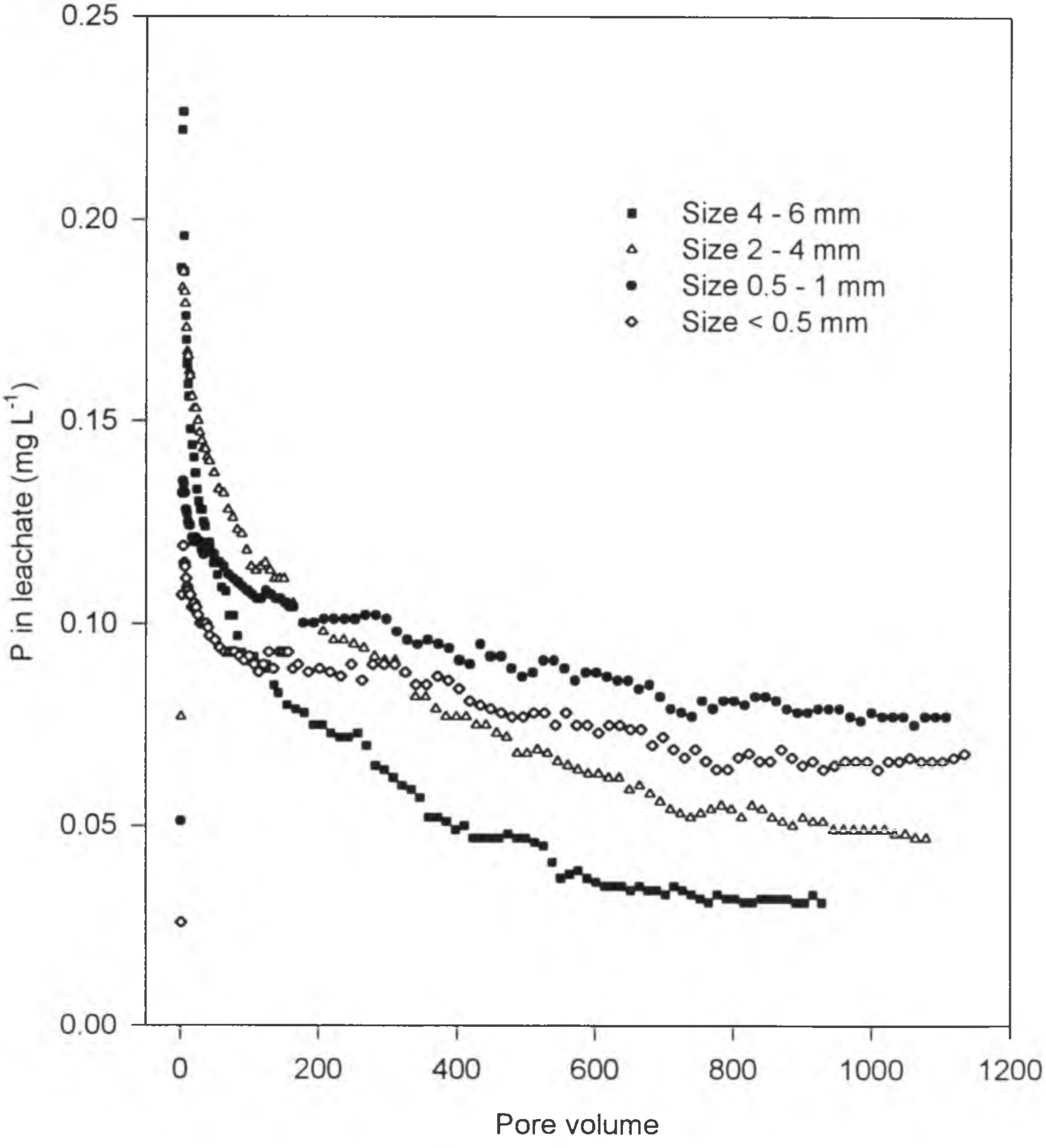

Figure 5.6. Effect of aggregate size on P in leachate, 800 mg P kg^{-1} was added to separated aggregates, Leilehua soil.

consequently, should initially increase solution P. On the other hand, the ratio of directly accessible reactive sites represented by the sample outer surface area in relation to the sample mass increases with decreasing aggregate diameter assuming a spherical aggregate size (Table 5.3). Thus more P release will be expected from small aggregates.

Table 5.3. Ratio of the "accessible" outer spherical surface to soil mass for differing aggregate fractions.

Size	Diameter[†]	ratio of outer surface to soil mass[‡]
---------------- mm	-----------------	$m^2\ kg^{-1}$
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 (3.1) (Addiscott et al., 1983, and Chapter 3).
[‡] Outer surface was calculated by equation (3.2).

Ion exchange processes between the inter- and intra-aggregate pore systems, and the nutrient uptake by roots depend not only on the accessible soil surface but also the on the amount of exchangeable ions in the aggregates on the basis of the surface area (Horn and Taubner, 1989). P desorption shown in Figures 5. 4 and 5.5 was calculated relative to aggregate mass. Results of an analogous analysis but based on the estimated outer surface area of aggregates are shown in Figures 5.7 and 5.8. Cumulative P release increased with increasing aggregate size.

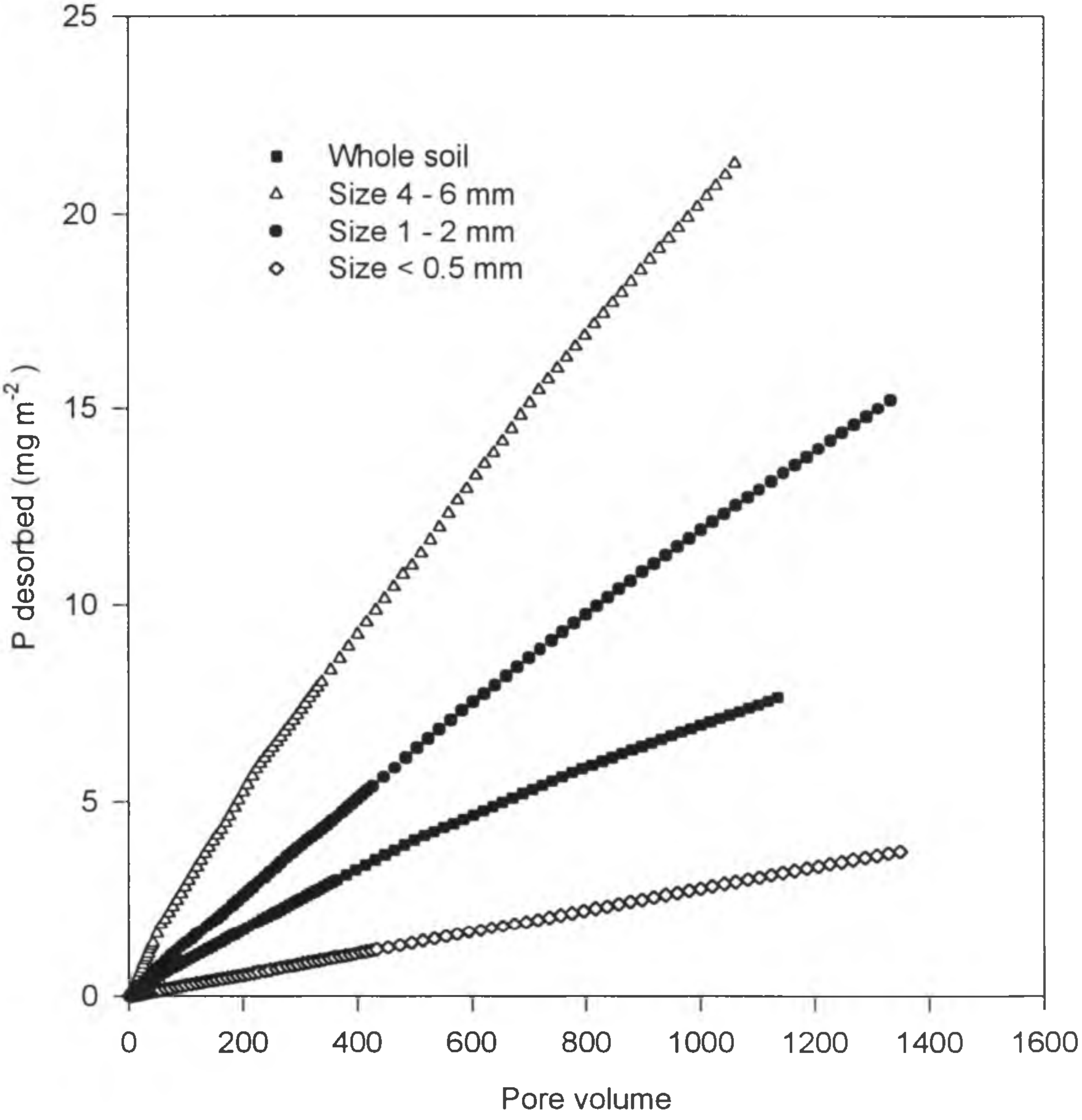

Figure 5.7. Phosphorus desorption per unit of estimated surface area from differing aggregate fractions. 800 mg P kg^{-1} was added to the mixture of differing aggregate fractions, Leilehua soil.

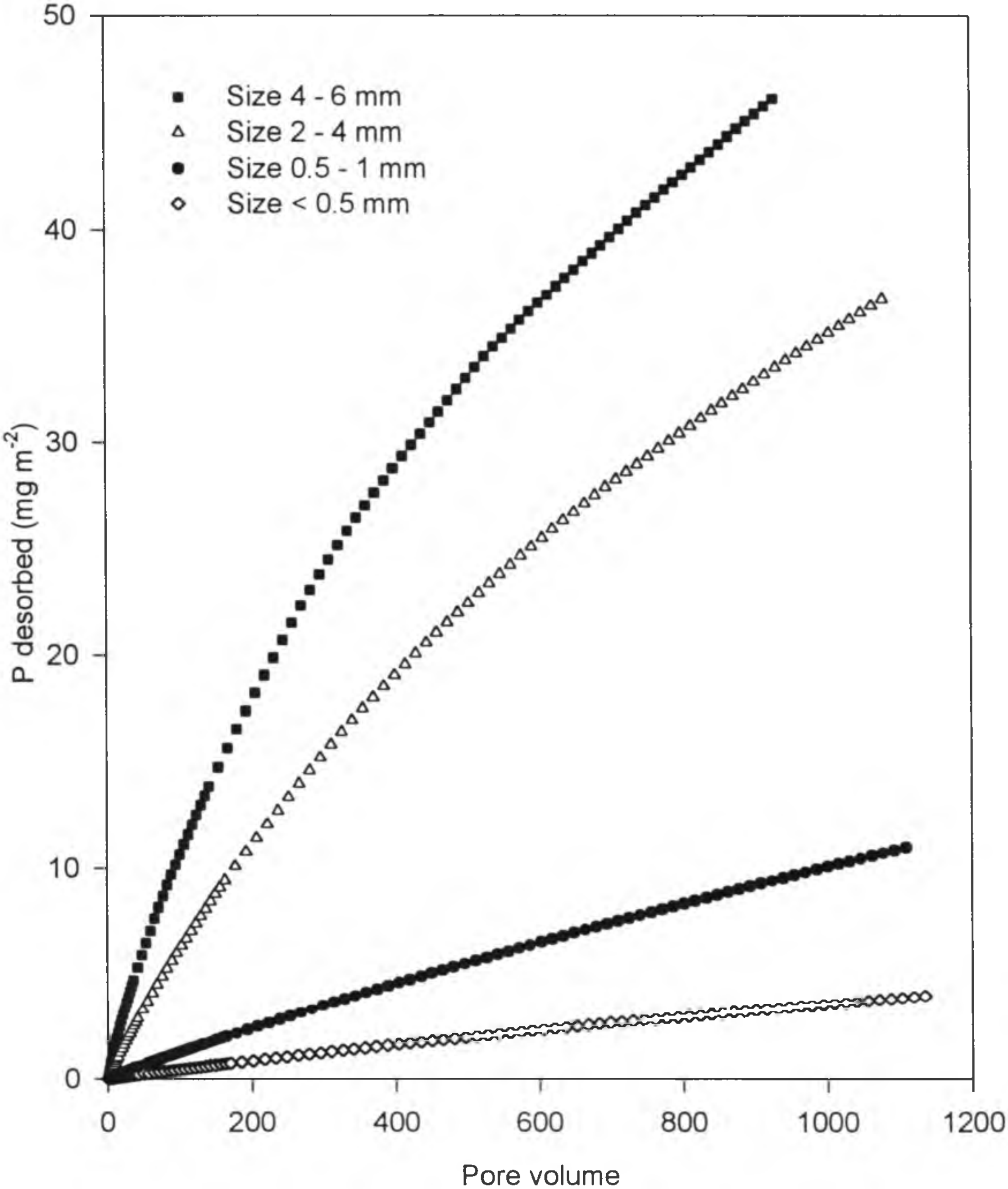

Figure 5.8. Effect of aggregate size on P desorption per unit of estimated surface area. 800 mg P kg^{-1} was added to separated aggregates, Leilehua soil.

Comparison of Kinetic Models

Several kinetic equations were evaluated with regard to their fit of the P desorption data using graphical and nonlinear regression procedures. Goodness of fit of the kinetic equations to the data was evaluated with the coefficient of determination (r^2) and standard error (Se) (Table 5.4). 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 solution. The diffusion layer may be the unstirred water film surrounding outer aggregate surfaces or water films on surfaces within the aggregate itself. Consideration of the low Se of the power function, the power function seems to be an improvement over the parabolic equation except for the Wahiawa soil and its aggregate fractions.

The simple Elovich equation was the poorest of 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. Examples of curve fits are presented in Figure 5.9. The superiority of the expanded equation over the simplified equation in describing P desorption has been documented (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 curve. This is probably one of reasons that the expanded

Table 5.4. Coefficients of determination (r^2) and standard errors (Se) for various kinetic equations for 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
Wahiawa soil								
Whole 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
Kapaa soil								
Whole 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
Leilehua soil								
Whole 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
P added to separated aggregates								
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

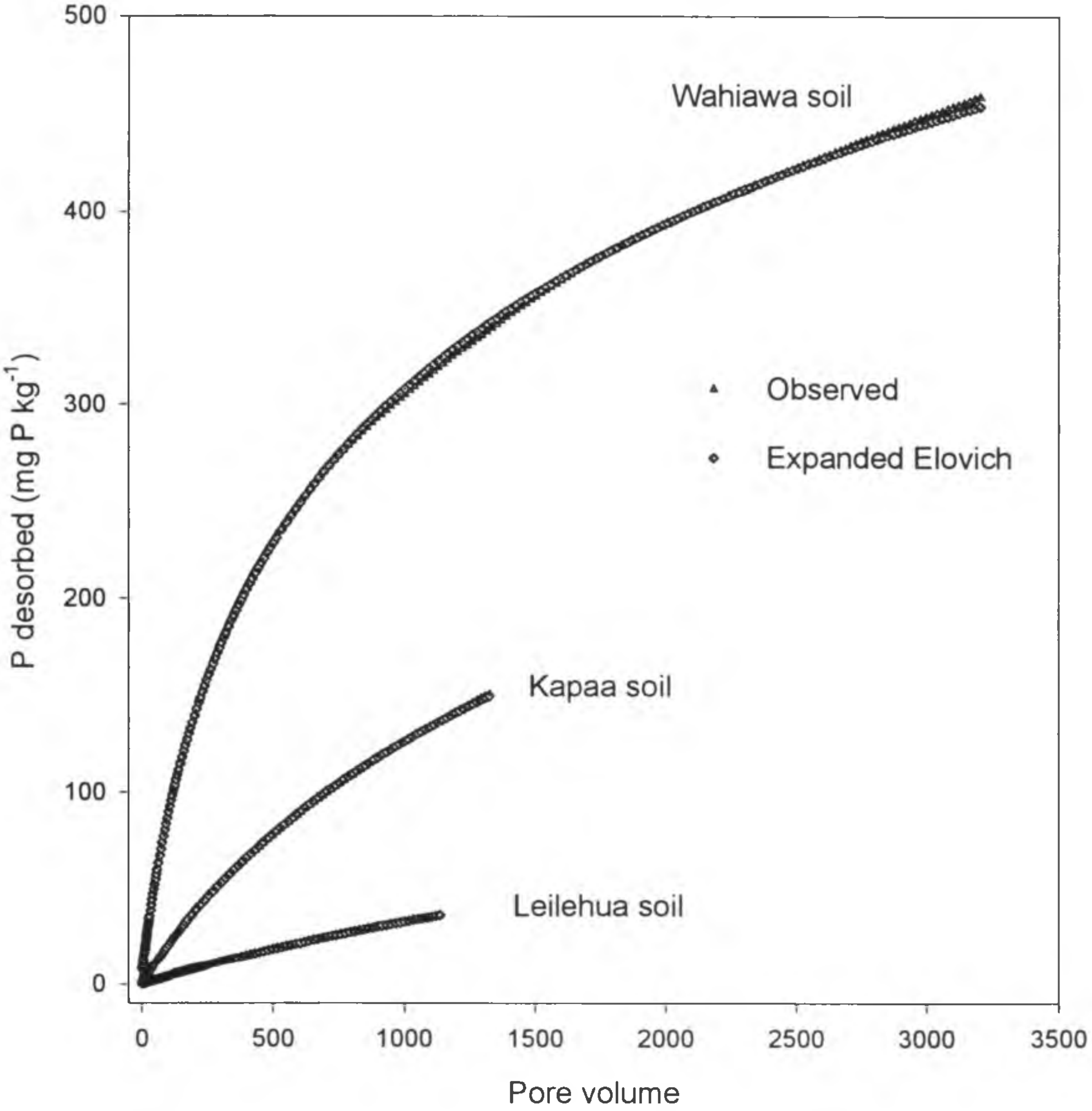

Figure 5.9. Phosphorus desorption curves fitted with the expanded Elovich equations.

Elovich equation fits the data so well in this study. It has been used previously to describe many kinetic processes including bulk and surface diffusion (Sparks, 1986; Allen et al., 1995), providing further evidence that P desorption is likely controlled by diffusion processes. 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).

Phosphorus Desorption Rate

The rates of P desorption from the soils and aggregate fractions were estimated from the expanded Elovich equation at 10 pore volumes, and plotted against aggregate size (Figure 5.10 a - d). Note that the diameter for 4-6 mm aggregates of the Wahiawa soil was re-estimated based on aggregate sizes and their aggregate size fractions after column leaching. This aggregate diameter was 1.378 mm (calculation not shown). The rate of P desorption decreased with increasing aggregate size after P was added to the whole soils (the Wahiawa and Kapaa soils) or the mixture of differing aggregate fractions (the Leilehua soil) (Figure 5.10 a - c). The rate of P desorption from subsequently separated aggregate fractions, however, increased with increasing aggregate size after P was individually added to separated aggregates after 10 pore volumes but subsequently decreased after 500 pore volumes (Figure 5.10 d).

Phosphorus in solution should be the same among aggregates after P is equilibrated with the whole soil or the mixture of differing aggregate fractions. Thus the

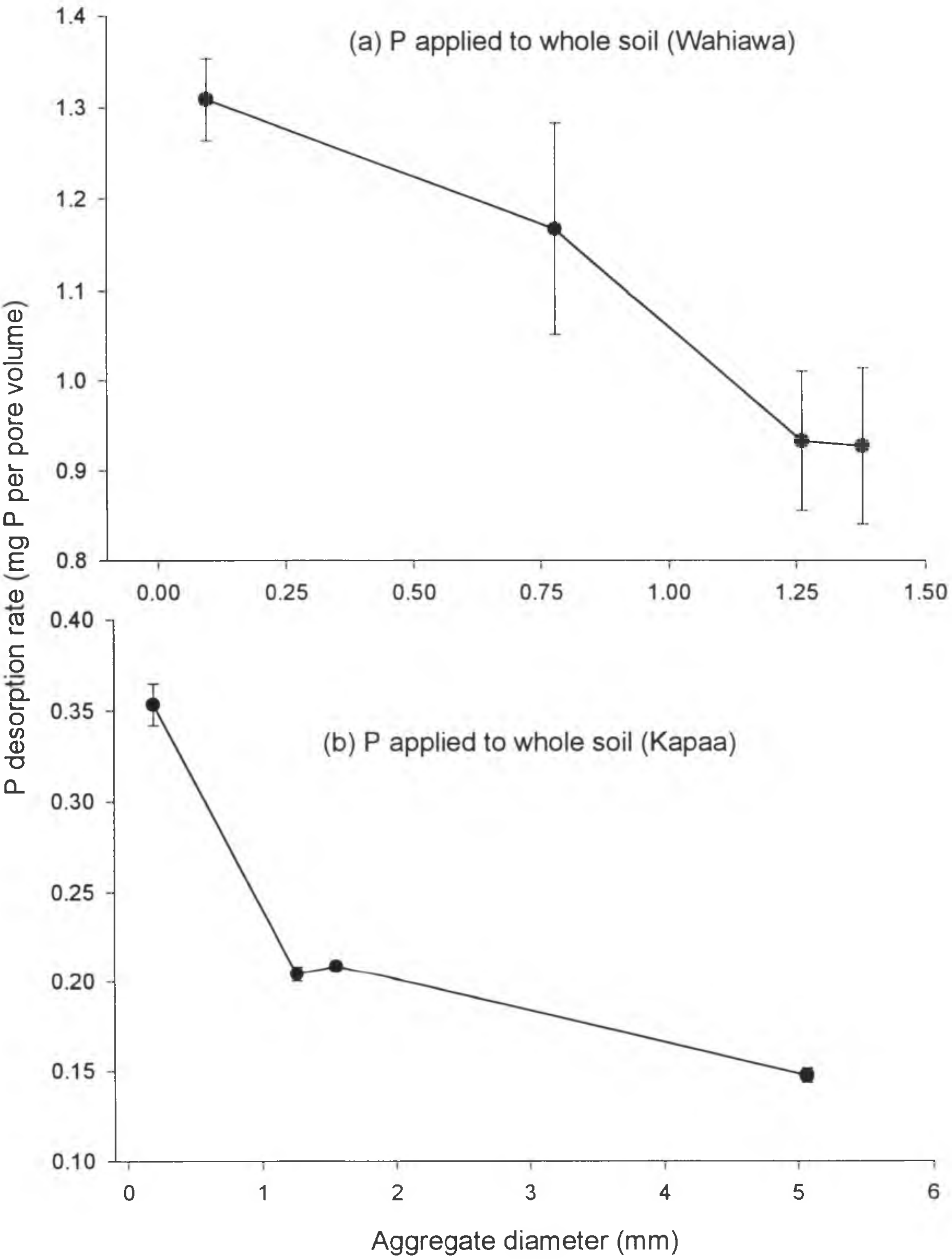

Figure 5.10. Effects of aggregate diameter on P desorption rate at 10 pore volumes. Error bars represent one standard deviation.

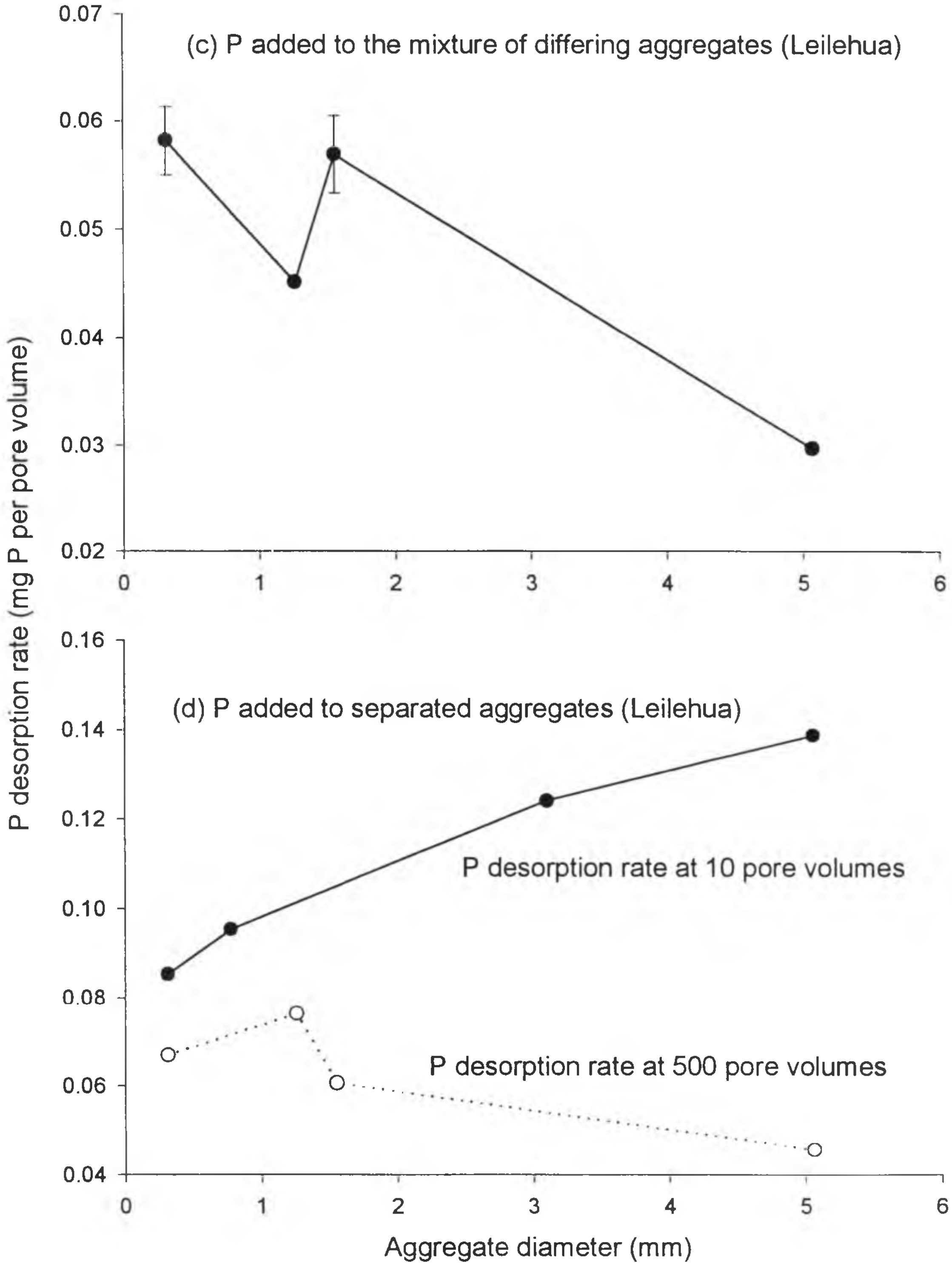

Figure 5.10 (Continued). Effects of aggregate diameter on P desorption rate at 10 pore volumes. Error bars represent one standard deviation.

decrease of rate of P release from aggregates separated from P-enriched soils with increasing aggregate size suggests that either the accessibility of reactive sites on the aggregate surface by leachate or P diffusion from the inside of aggregates probably control P release from aggregates for a given soil. After P was individually added to separated aggregates, the solution P obtained from the large aggregates was greater than that with small aggregates (see Chapter 4). Thus there was either more P release or less P sorption on the large aggregates. The greater rate of P desorption on the Leilehua soil at 10 pore volumes may reflect the greater solution P concentration in large aggregates. With increased leaching, solution P is removed and decreases. Then the accessible reactive sites on the aggregates and P diffusion from aggregate interiors should become more important in controlling P desorption, consequently, leading to a decrease in P desorption rate at 500 pore volumes (Figure 5.10 d). The rates of P desorption at 500 pore volumes (estimated from the expanded Elovich equation) were 0.067, 0.076, 0.061, and 0.046 mg P per pore volume for the aggregate fractions of size < 0.5, 0.5-1, 2-4, and 4-6 mm, respectively (Figure 5.10 d), illustrating the reduced desorption from large aggregates after extended leaching.

Effects of Aggregate Size on Phosphorus Supply in the Leilehua Soil

The total P content of shoots and root dry weights of soybean and lettuce was significantly influenced by aggregate size and P additions (Table 5.5). There were

Table 5.5. ANOVA table for total P in shoots and root dry weight.[†]

Treatment	df	Soybean				Lettuce			
		P content (mg P pot^{-1})		Root dry weight (g pot^{-1})		P content (mg P pot^{-1})		Root dry weight (g pot^{-1})	
		Mean Sq[‡]	F	Mean Sq	F	Mean Sq	F	Mean Sq	F
Aggregate Size	3	1.058	17.69^{**}	0.120	7.05^{**}	3.75	30.34^{**}	4.33	71.21^{**}
P rate	4	9.480	158.50^{**}	0.252	14.83^{**}	41.18	332.80^{**}	25.36	416.60^{**}
Size x P rate	12	0.213	3.56^{**}	0.0300	1.77^{ns}	0.321	2.60^{ns}	0.314	5.16^{**}
Block	2	0.0985	1.65^{ns}	0.0259	1.52^{ns}	0.155	1.25^{ns}	0.105	1.73^{ns}
Residual	38	0.0598		0.0170		0.124		.0609	

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

[‡] Mean Squares.

** Significant at $p \leq 0.01$.

ns Not significant at $p \leq 0.05$.

interactions between P addition and aggregate size for the total P content of soybean shoots and the root dry weight of lettuce.

1)Total Phosphorus in Shoots

The total P contents of soybean and lettuce shoots of plants grown in large aggregates (2-6 mm) were greater than those of plants grown in small aggregates (< 0.5 mm) when P was individually added to separated aggregate fractions during the short growth period of 30-32 days (Figure 5.11 and 5.12). For soybean, however, the effects of aggregate size on the P content in soybean shoots was dependent on P rate because there significant interaction between aggregate size and P rate. The difference in P content in soybean shoots between the 2-6 mm aggregate fraction and the < 0.5 mm aggregate fraction increased with increased applied P levels (Figure 5.11). The total P contents in soybean and lettuce shoots of plants grown in the whole soil were within the bounds between <0.5-mm aggregates and 2-6-mm aggregates for all P additions (Figure 5.11 and 5.12). The decrease in extractable P from large aggregates after harvest was also greater than the decrease from small aggregates (data not shown). The difference in soil extractable P before planting and after harvesting was calculated and the relationship between the total P in shoots and the difference in extractable P is shown in Figure 5.13. The change in soil extractable P was a better prediction of P in shoots in soybean than in lettuce (Figure 5.13). It should be noted that not only P uptake by soybean and lettuce but also the continuous reaction between the added P and soil components during the plant

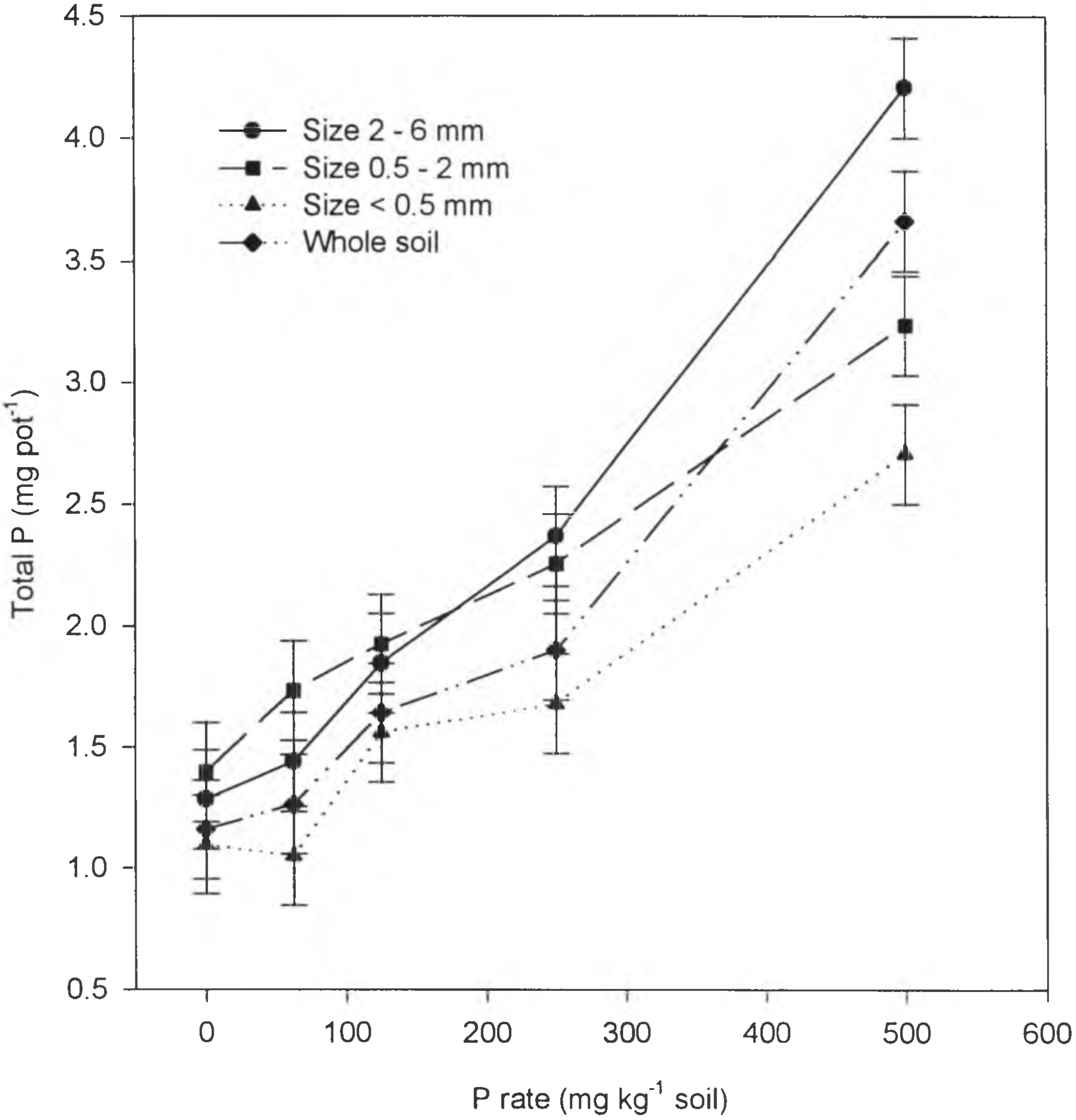

Figure 5.11. Effect of aggregate size on total P in soybean shoots on the Leilehua soil. Error bars represent one LSD at $p \leq 0.05$.

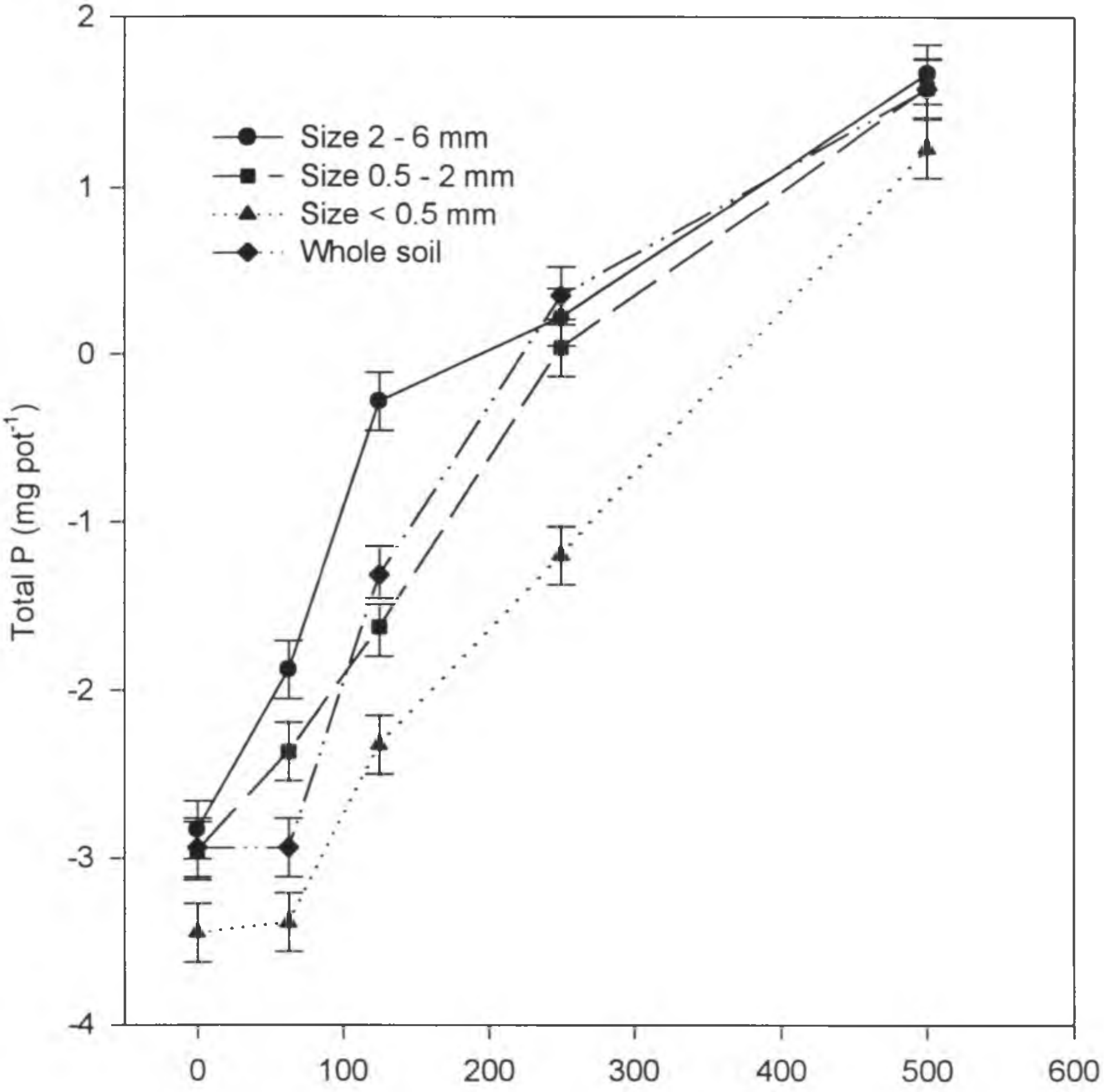

Figure 5.12. Effect of aggregate size on total P in lettuce shoots on the Leilehua soil. Error bars represent one LSD at $p \leq 0.05$. The total P in shoots was logarithmically (natural) tranformed.

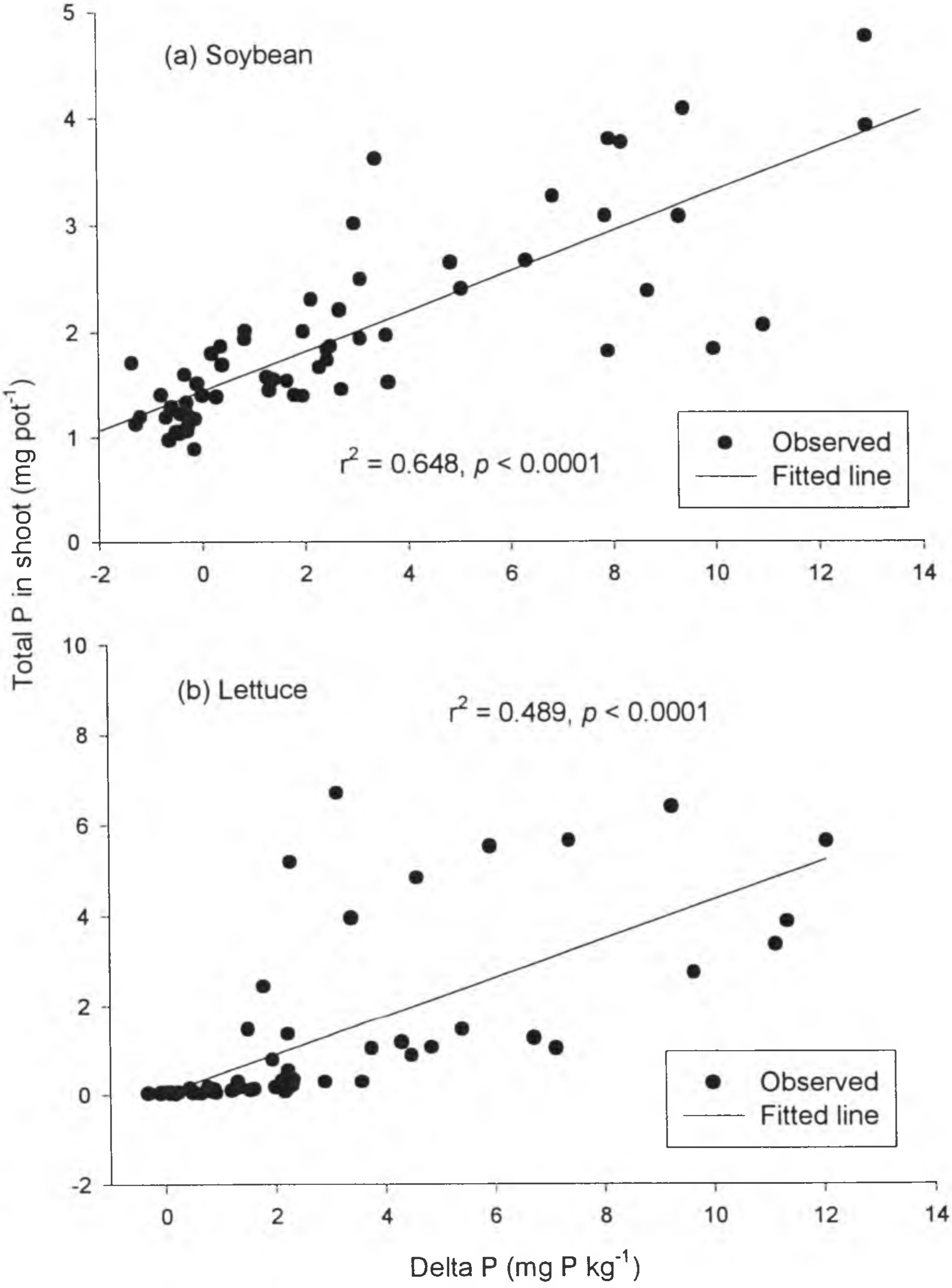

Figure 5.13. Relationship between total P in shoots and difference in 0.5 *M* $NaHCO_3$ extractable P before planting and after harvesting (Delta P).

growth period probably contributed to the decrease in extractable P. The decrease in extractable P with time was reported and more fully discussed in Chapter 4.

The greater total P in plant shoots grown in the large aggregate fraction corresponded with the initial greater rate of P release from this fraction after P was added to separated aggregate fractions in the laboratory study. In this laboratory study, P sorption was reduced in large aggregates and P desorption increased. Thus more P was available to plants from large aggregates when P was added to the separated aggregates.

A greater decrease in P desorption rate with increased leaching, however, was observed from large aggregates than from small aggregates. This suggested that P uptake by plants would be small from large aggregates after most of easily desorbed P was removed. With depletion of P around the aggregates, P diffusion from the inside of the aggregates to the outside, or/and the accessibility of roots to P within the aggregates are hypothesized to become an important influence on P uptake by plants.

2) Root Growth

Dry weights of roots grown in small aggregates (< 0.5 mm) were less than that of plants grown in large aggregates (2-6 mm) for both soybean and lettuce for all but the 0 P treatment for soybean (Table 5.5, Figure 5.14). Differences in root growth among aggregate fractions with size 0.5-2, 4-6 mm, and whole soil (< 2 mm) were small.

The increase in root growth with increasing aggregate size was not consistent with the results reported by Misra et al. (1988a) that the root growth in beds of larger

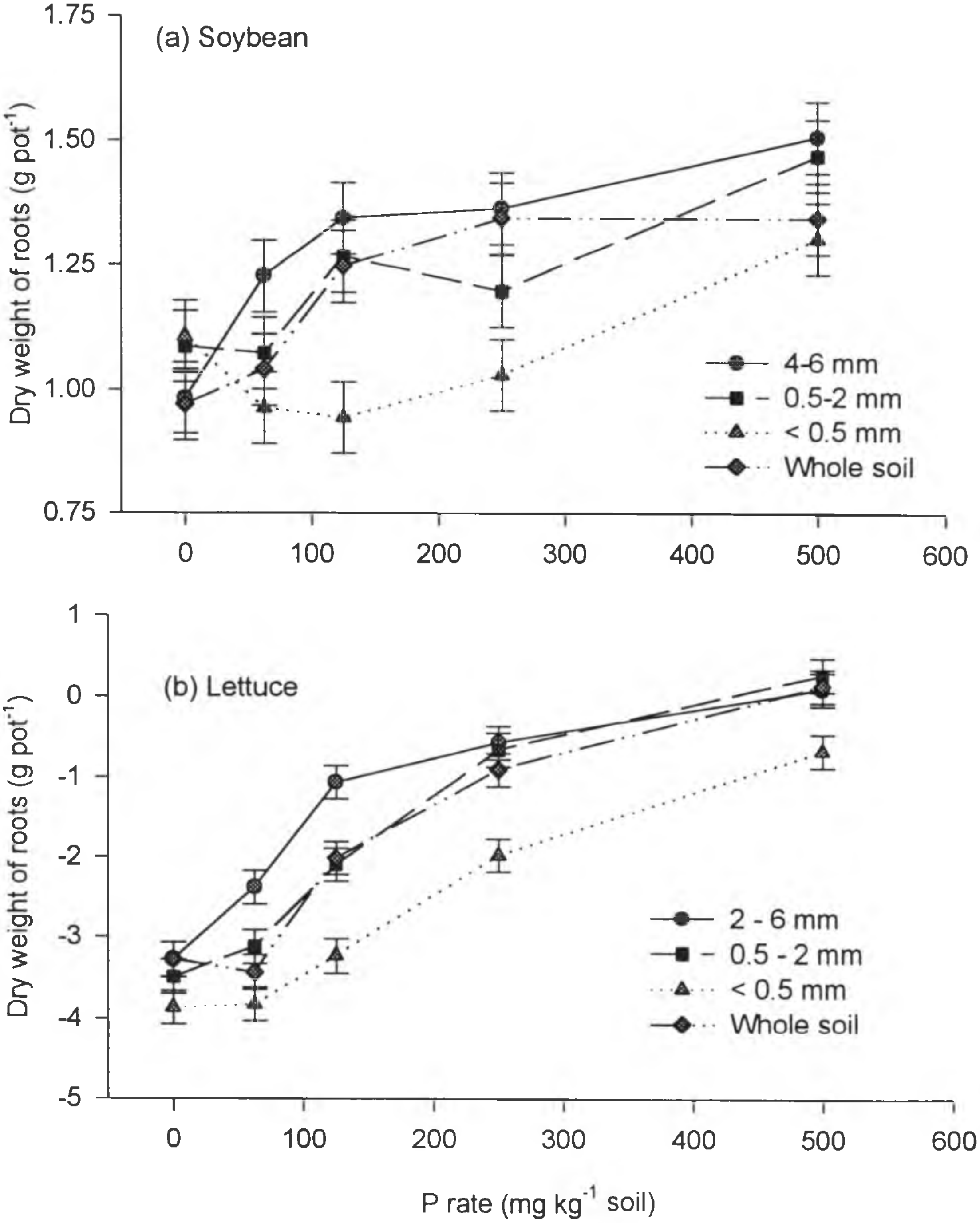

Figure 5.14. Effect of aggregate size on dry weight of plant roots on the Leilehua soil. Error bars represent one LSD at $p \leq 0.05$. The dry weight of roots for lettuce was logarithmically (natural) tranformed.

aggregates was lower than in beds of small aggregates. They concluded that the reduced root growth was due to greater impedance to root penetration. In a simulation study, Misra et al. (1988b) demonstrated that P uptake by roots growing within aggregates should be higher than uptake by roots growing on the surface of aggregates. Thus the distribution of roots in aggregates is predicted to influence P uptake by roots.

The greater root growth of plants growing in large aggregates may be due to the available P status in soils. In this experiment, P was added to the separated aggregate fractions, and the available P in larger aggregates was greater than in smaller aggregates. If P was limiting, the increased root growth due to more available P in the large aggregates may have compensated for decreased root growth due to greater mechanical impedance to root penetration. The interaction between aggregate size and P addition for lettuce may be related to such an effect. The difference in root growth between the largest aggregates (2-6 mm) and the smallest aggregates (< 0.5 mm) was greatest at a P addition rate of 125 mg P kg^{-1} for both lettuce and soybean (Figure 5.14), when aggregate size could affect the P availability but P would still would be limiting.

The results here suggest that some soil P requirement procedures may over-estimate P fertilizer requirements by under-estimating soil P status because diffusion-limited P sorption sites are exposed due to grinding and shaking soil samples during laboratory analysis. For example, the P requirement to attain solution P of 0.03 mg P L^{-1} using the Fox and Kamprath method was 100 mg P kg^{-1} greater than the P requirement estimated with undisturbed (natural) soils for the Haiku soil (Linquist et al., 1995).

Cassman et al. (1993) found that an application of 100 kg P ha^{-1} to the Haiku soil produced maximum yield, although the recommended P application rate, based on the Fox and Kamprath method, was more than 500 kg P ha^{-1} (Cassman et al., 1981).

The reduced P sorption and increased P desorption with increasing aggregate size suggests that an improved prediction of the P buffer coefficients would be achieved by including aggregate size. Thus considerations of the aggregate effects for some current P requirement procedures could improve quantifying the relationship between extractable P, P supply, and crop yield.

CONCLUSIONS

Phosphorus desorption was initially greater from large aggregates (4-6 mm) than from small aggregates (< 0.5 mm) after P was individually added to separated aggregates. Phosphorus desorption from large aggregates, however, decreased faster than from small aggregates with additional leaching. When P had been added to the whole soils (the Kapaa and Leilehua soil) and a mixture of differing aggregate fractions (the Leilehua soil), however, P desorption from subsequently separated large aggregates was less than from small aggregates. The outer surface area of soil aggregates and diffusion of P from the interior of soil aggregates to the exterior are hypothesized to control P adsorption and desorption.

Soybean and lettuce were grown in varying-sized aggregates (whole soil, < 0.5, 0.5-2, 2-6 mm) to assess the P availability. The total P in soybean and lettuce shoots, and the root dry weights grown in larger aggregates (2-6 mm) was greater than in soybean and lettuce grown in smaller aggregates (<0.5 mm) after P was added to separated aggregate fractions. The changes in root dry weight of soybean and lettuce were consistent with the greater total P in shoots grown in larger aggregates.

The results point out the inability of some soil P requirement procedures to evaluate the effects of P diffusion in aggregates, desorption, and accessibility of root systems to P within the aggregates on soil P supply. Adapting current procedures in light of aggregate effects could improve quantifying the relationship between extractable P and crop yield. The results also suggest that an increase in soil aggregation increases P availability. Thus soil managements, such as cropping system, tillage method, which affect soil aggregation, would influence soil P availability.

CHAPTER 6 SUMMARY AND CONCLUSIONS

The influence of soil aggregate size on P availability was evaluated in Typic Kandihumult (Leilehua), Anionic Acrudox (Kapaa), and Rhodic Eutrustox (Wahiawa), with an incubation study, a leaching column study, and a pot experiment. These soils represent high P sorption and a range in soil aggregation.

Positive relations of the geometric mean diameter and weighted mean diameter of water-stable aggregates to the content of soil amorphous material estimated by the Rietveld method were found in highly weathered soils. Among other factors that influence soil aggregation may be the ratio of $SiO_2/(Al_2O_3 + Fe_2O_3)$, organic carbon, and crystalline minerals in the soils. The 30 - 40 % of total porosity filled with water at 1.5MPa of suction in the Leilehua, Kapaa, and Wahiawa soil were attributed to the presence of intra-aggregate pores. Existence of such pores (2 - 3 μm in width) was verified with the aid of a scanning electron microscope for the Leilehua soil. The significance of the intra-aggregate pores may lie in increased soil surface area and in increased water and nutrient retention. Improved understanding of nutrient retention and transport of nutrients and hazardous solutes in such aggregated soil should improve nutrient management and protect our environment.

For the Kapaa and Leilehua soils, sodium bicarbonate extractable P increased up to 5-fold with decreasing aggregate size when P had been added to soils for 3 - 7.5 years. The extractable P did not increase with decreasing aggregate size on all soils where no

P had been applied and even where P had been applied to the Wahiawa soil. Organic P in aggregates did not change with increasing aggregate size in either the control or P-added treatments on the Leilehua soil. The differing outer surface area of aggregates alone did not explain the change in extractable P with aggregate size. An incubation study indicated that the increase in extractable P with decreasing aggregate size was probably due to increased sorbed P in aggregates. The lack of a relationship between extractable P and aggregate size in the Wahiawa soil may be related to the low aggregate stability of the Wahiawa soil compared to the Kapaa and Leilehua soils. The change in extractable P with aggregate size suggests that soil aggregation may affect P sorption and P availability.

By contrast, P sorption decreased, 0.5 *M* $NaHCO_3$ extractable P, and 0.001 *M* $CaCl_2$ extractable P increased as aggregate size increased after P was added to separated aggregate fractions. Phosphorus desorption was initially greater from large aggregates (2-6 mm) than from small aggregates (< 0.5 mm). The total P in soybean and lettuce shoots, and the root dry weights grown in the large aggregates (2-6 mm) were higher than in the small aggregates (<0.5 mm). The increased P uptake by crops with increasing aggregate size was due to increased P desorption from aggregates through reduced P sorption. The results suggest that an increase in soil aggregation reduces P sorption, and increases extractable P. Thus grinding and shaking soil sample used in P analysis may over-estimated P requirements by under-estimating soil P availability because diffusion-limited P sorption sites are exposed to increase P sorption. Soil managements that favor soil aggregation would increase P availability and may be considered in P management decisions.

The results point out the inability of some current soil tests to evaluate the effects of P diffusion in aggregates and accessibility of root system to P within the aggregates on soil P supply. Adapting current soil test procedures in light of aggregation effects could improve predicting P requirement in food and fiber production.

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