Effects of fertilisation on phosphorus pools in the volcanic soil of a managed tropical forest

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ABSTRACT

Acacia koa forests benefit from phosphorus fertilisation, but it is unknown if fertilisation is a short or long term effect on P availability. Past research suggests that P cycling in soils with high P sorption capacity, such as Andisols, was through organic pathways. We studied leaf P and soil P fractions in a tropical forest Andisol for 3 years after fertilisation with triple super phosphate. Leaf P concentration and labile P remained high after fertilisation. Fertilisation had increased all the inorganic P fractions over the length of the study, while organic P fractions had not. The results suggested that the organic P fractions had a reduced role as a source of labile P after fertilisation. The size and dynamics of the sodium hydroxide- and hydrochloric acid-extractable P pools would suggest that either pool could be major sources of labile P. Because of the high level of poorly crystalline minerals in Andisols (allophone and imogolite), it would be expected that applied P would quickly lead to strong P sorption onto mineral surfaces and thus a rapid decline in P availability. We propose that the high organic matter present in these soils had masked some of the Al and Fe sorption sites, which allowed the sorption and desorption when large amounts of addition P were applied.

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1. Introduction

The endemic tree species Acacia koa (A. Gray) is an important hardwood in Hawaii. The natural range of this keystone species is from 100 to 2300 m elevation and from 850 to 5000 mm mean annual precipitation (Elevitch et al., 2006). The species was extensively cleared after European contact, and today it is estimated that koa covers only 10% of its historic range (Wilkinson and Elevitch, 2003). Recently, interest in reforestation of koa has dramatically increased for ecological, cultural, and commercial reasons. However, koa was never assessed for commercial management, and only a few studies have assessed nutrient requirements or responses to fertilisation. Phosphorus (P) has been identified by several studies as a limiting factor for koa growth and development (Cole et al., 1996; Scowcroft and Silva, 2005; Scowcroft et al., 2007). Pearson and Vitousek (2001) showed no response to nitrogen (N) fertilisation but hypothesized that P may be a limiting nutrient as young stands develop and sequester sparingly available soil P in plant biomass. A recent silviculture study showed that koa thinning combined with exotic grass control and heavy P fertilisation could double koa diameter growth

rates (Scowcroft et al., 2007). Although short-term increases in soil P availability were measured, there has been no examination of the long-term effects of P fertilisation or a broader study of the P cycle in koa forests.

The phosphorus cycle is complex, with many sources and sinks in various biogeochemical pools. Measuring labile P in soil extractions has often failed to provide a satisfactory index of soil P fertility. It can be difficult to find a strong correlation between foliar nutrient concentrations, labile soil P, and tree productivity (Smethurst, 2000; Schuur and Matson, 2001). When such correlations can be established, it is normally specific to site and tree species (Fisher and Binkley, 2000; Smethurst, 2000). Further, the concept of a critical nutrient concentration for plant growth seems not to hold in many forest situations (Fisher and Binkley, 2000; Will et al., 2002). Thus, for a better understanding of soil P availability and plant and soil responses to fertilisation or other forms of forest management, a more complete picture of the P cycle is required. One approach is to examine soil P pools that are a part of P cycling pathways relevant for plant uptake. An example of this is the Hedley fractionation, which is the sequential extraction of P from soil that provides a measure of various inorganic and organic P pools with decreasing availability to plants (Hedley et al., 1982). The Hedley fractionation has become widely used to determine changes in P pools over time, vegetation, environment, and management (Tiessen et al., 1984; Cross and

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Schlesinger, 1995; Thomas et al., 1999; Jin et al., 2000; Nguyen et al., 2001; Vinegla et al., 2006).

In Hawaii, volcanically derived soils range from newly formed to over 4 million years old, and for most of their development the soil minerals have a high potential for labile P to be sorbed and made unavailable to plants (Fox and Searle, 1978; Jackman et al., 1997; Wang et al., 2000). Previous studies in Hawaiian forests dominated by the native tree *Metrosideros polymorpha* (Gaud.) have shown that a deficiency of labile P on highly weathered soils (Vitousek et al., 1988; Crews et al., 1995; Herbert and Fownes, 1999; Hedin et al., 2003). Studies in koa-dominated forests in Hawaii have also indicated that labile P was low (Harrington et al., 1995; Ares and Fownes, 1999), even on younger soils with high reserves of primary mineral P (Idol et al., 2007). Andic soils have a high P-sorption capacity due to the very high surface area of allophanic and amorphous minerals (Shoji et al., 1993). On these soils, one would expect any increase in labile P after fertilisation to be fleeting. In the silvicultural study reported by Scowcroft et al. (2007), P fertiliser effects on growth rates were still significant several years after the last P application. The response clearly showed that koa growth is limited by low plant available P; however the nature of the effect of P fertilisation on koa forest soils is unknown. In these soils, one would expect that any P applied would be quickly sorbed to the minerals and become biologically unavailable for plant access. Any long-term fertiliser effect would require uptake by the plants or sorption by other pools that allow for active cycling within the system. More information about the P cycle is needed to better understand the lingering effect of P fertilisation on koa growth in these young Andisols.

The objectives of this study were to (1) quantify changes in soil P pools with silvicultural treatments; (2) determine if there was a long-term effect on labile P; and (3) determine if P fertilisation had changed P cycling within the soil.

2. Materials and methods

2.1. Site description

The study site was located on the eastern slopes of Mauna Loa Volcano on the Island of Hawaii (19° 31′ 12″ N, 155° 19′ 14″ W), between 1650 and 1740 m above sea level. Mean annual precipitation for the site between 2002 and 2005 averaged 1740 mm with a mean annual 24-h air temperature of 12.1 °C (Scowcroft, unpublished data). The site is classified as a subtropical lower montane wet and moist forest (Tosi et al., 2002). The preliminary soil description of the dominant soil type is the Keamoku series, a medial-skeletal, amorphic, isomesic Typic Hapludand (NRCS, 2008). The well drained, silt loam soils formed on large deposits of basic volcanic ash over basic aa lava (1500–3000-year-old), with an average soil depth of 20–40 cm (Scowcroft et al., 2007). They also have high organic carbon and low pH (Table 1). The study site was within an area of degraded mature forest dominated by *A. koa* and *M. polymorpha* that was used for extensive cattle grazing until the site was logged in 1978. The entire overstory was removed, and then the soil was scarified by bulldozer to encourage regeneration of koa from the soil seed bank.

Exotic grass species invaded the forest floor and developed thick mats as the forest regenerated. These species included kikuyu grass (*Pennisetum clandestinum* Chiov.), meadow rice grass (*Erharta stipoides* Labill.), and sweet vernalgrass (*Anthozanthum odoratum* L.). Currently, koa dominates the overstory, and a mixture of native woody species and ferns are present in the understory, although meadow rice grass is still prominent.

2.2. Experimental design of the koa silvicultural study

For a complete description of the experimental design and its establishment, see Scowcroft et al., 2007. The experiment employed a split-plot design with targeted thinning as the main treatment and grass control and fertilisation as the sub-plot treatments. Eight 60 m × 60 m main treatment plots were established, and potential crops trees were selected in each plot based on size and stem form. Four replicates of the thinning treatments were randomly assigned. The thinning treatment was accomplished by double girdling koa trees that immediately surrounded the selected crop trees. Within each main treatment plot, four 25 m × 25 m subplots were established. There was a 5-m buffer between plots. Three of the four sub-plots were randomly selected for two sub-plot silvicultural treatments and a control. The herbicide (H) treatment involved chemical control of exotic grasses. In May 2002, all grasses within a 2-m radius of each selected crop tree were sprayed with an application of Fusilade® DX (Syngenta Professional Products, Greensboro, NC) according the manufacturer's instructions at a rate of 0.42 kg active ingredient (Fluazifop-P-butyl) ha^{-1}. Periodic spot spraying ensured that the exotic grasses did not re-establish within the area. The fertiliser treatment (HF) was combined with the herbicide treatment using applications of a P fertiliser. In November 2002, triple super phosphate was broadcast by hand evenly throughout the entire sub-plot, at a rate of 300 kg P ha^{-1}. Three additional applications of fertiliser were applied every 6 months at 150 kg P ha^{-1}. A total of 750 kg P ha^{-1} was applied over a period of 2 years. There was no fertiliser-only sub-plot treatment.

2.3. Live leaves

Mature, full-sun, live leaves (phyllodes) were sampled by pruning pole in the top third of the canopy in February 2004 and September 2007. Phyllodes are the swollen rachis of a compound leaf that replaces true leaves in mature koa trees. Three crop trees were randomly selected in each sub-plot, and for each selected tree, three different branchlets were cut and five phyllodes were sampled per branchlet. All plots were sampled in 2007, while for 2004 only two unthinned plots and two thinned plots were sampled. Samples were dried at 70 °C for at least 3 days before being ground with a Wiley Mill through a number 40 mesh (0.5 mm) screen. The ground leaves were sent to the University of Hawaii-Manoa Agriculture Diagnostic Service Center for P analysis by inductively coupled plasma (ICP) emission spectroscopy. Samples were prepared for ICP by adding 0.5 g of the dry ground sample to 5 mL concentrated HNO_3 and digested on a preheated block at 150 °C.

Table 1
Soil properties at Keauhou Ranch Soil pH was measured with a 2:1 ratio of deionised water to air dried soil by sub-treatments: control (C), herbicide (H), and H + phosphorus fertiliser (HF). Standard error in parentheses.

Sub-trt	pH_W		Carbon content (%)		Nitrogen content (%)		C:N ratio	
	Unthinned	Thin	Unthinned	Thin	Unthinned	Thin	Unthinned	Thin
C	4.31 (0.05)	4.18 (0.04)	37.3 (3.2)	39.1 (1.9)	2.5 (0.2)	2.6 (0.1)	15.2 (0.2)	15.1 (0.2)
H	4.15 (0.01)	4.09 (0.05)	41.4 (1.7)	38.1 (1.7)	2.7 (0.1)	2.5 (0.1)	15.2 (0.3)	15.0 (0.4)
HF	4.56 (0.29)	4.22 (0.07)	37.8 (1.6)	38.9 (2.3)	2.5 (0.1)	2.5 (0.1)	15.2 (0.4)	15.6 (0.4)

2.4. Hedley fractionation

In March 2005, 2006, and 2007, soil samples were taken from each sub-plot. Soil was collected within 2 m of five randomly selected crop trees and bulked within each sub-plot. Samples were collected at the 5 cm depth only. Soils were placed in polyethylene bags, transported on ice to the laboratory, and then stored at 4 °C. Before analysis, soils were air-dried and then sieved through a 2-mm mesh screen.

Soil P fractions were analyzed using the Hedley et al. (1982) sequential extraction method as modified by Tiessen and Moir (1993). This method extracts P pools in decreasing order of biological availability and cycling rates from inorganic (Pi) and organic (Po) pools. Although there are other P pools, the Hedley fractions examined in this study are assumed to represent P pools that are the most biologically relevant (Tiessen and Moir, 1993; Richter and Markewitz, 2001). For the first extraction, an anion-exchange resin membrane (PRS-probe, Western Ag Innovations, Saskatoon, Canada) was used to sorb labile P. Approximately 0.5 g of oven-dry equivalent soil was mixed with 17.5 ml of ultrapurified deionised water and placed into a rectangular polyethylene bag. A single anion-exchange resin probe was added to the bag. Air was expelled from the bag, and it was sealed at the open end. The soil–water–resin mixture was gently shaken on a shaker table for 16 h. The soil was then recovered through centrifugation and filtration using a Millipore polyethene Nulceopore filter under light suction. The probe was washed and eluted in 35 ml of 0.5 M HCl and the extract retained for analysis of available inorganic P (resin Pi). Next, 30 mL of 0.5 M $NaHCO_3$ was added to the recovered soil and shaken for 16 h. The solution was centrifuged at $1450 \times g$ for 10 min and the supernatant recovered for P analysis. Centrifugation was used in subsequent steps to separate the extractant from the soil. Thirty mL of 0.1 M NaOH was added to the pellet, shaken for 16 h, centrifuged, and the supernatant recovered. Finally, 30 mL of 1 M HCl was added and the same steps were followed To remove organic matter from the $NaHCO_3$ and NaOH fractions for inorganic P analysis, an aliquot was acidified and then centrifuged $1450 \times g$ for 15 min before recovering the supernatant. Due to the high organic matter content of the soil, this step was not sufficient to clear these fractions for analysis. We added acid-washed activated charcoal to the acidified extracts and shook them gently for 10 min on a shaker table to sorb the remaining organic matter (Olsen and Sommers, 1982). After centrifugation, the supernatant was recovered for inorganic P analysis. Tests revealed no significant change in soluble orthophosphate due to the addition of activated charcoal. For the original $NaHCO_3$ and NaOH extracts, total P was determined by digesting the extract with ammonium persulfate (Tiessen and Moir, 1993). Organic P in these fractions (bicarbonate Po and hydroxide Po) was calculated as the difference between total P and the extracted inorganic fraction. Extracts from all the fractionation steps were analyzed using the citric acid-molybdate colorimetric procedure on a UV–visible spectrophotometer (Murphy and Riley, 1962).

The resin-extractable Pi fraction is believed to be immediately available for plant uptake. The bicarbonate-extractable Pi fraction is thought to readily desorb from soil surfaces, while hydroxide Pi represents non-occluded P strongly held to exchange sites associated with aluminium (Al) and iron (Fe) oxides. Exchange of sorbed P on these sites are assumed to have a slow turnover of labile P (Cross and Schlesinger, 1995). Finally, the acid extractable fraction is assumed to represent primary mineral P. The organic fractions represent P incorporated in or associated with biological material-including organic matter and micro-flora and -fauna. Bicarbonate Po represents organic P that can readily mineralize, while hydroxide Po is non-occluded P that is made available much more slowly (Cross and Schlesinger, 1995).

2.5. Phosphatase activity

Phosphatases describes a broad range of enzymes that have been classified into five major groups: phosphoric monoester hydrolases, phosphoric diester hydrolases, triphosphoric monoester hydrolases, enzymes acting on phosphoryl-containing anhydrides, and enzymes acting on P-N bonds (Florkin and Stotz, 1964; Tabatabai, 1994). This study concentrated on the most common class of phosphatases, phosphomonoesterases. The activity of these enzymes was assayed using disodium p-nitrophenyl phosphate as the substrate to induce mineralisation to inorganic P (Tabatabai and Bremner, 1969; Eivazi and Tabatabai, 1977; Tabatabai, 1994). This assay was performed on soils collected in March 2007. Samples were analyzed within 48 h of sampling. Two ∼1.3 g field moist sub-samples were taken from each sub-plot and placed in a 125-mL Erlenmeyer flask. One of the sub-samples was buffered at a pH of 6.5 with a modified universal buffer solution to provide the optimal conditions for acidic phosphatase activity and the second sub-sample was buffered at a pH of 11.0 for alkaline phosphatase activity. After buffering, 0.2 mL toluene, 4 mL modified universal buffer at the appropriate pH, and 1 mL of disodium p-nitrophenyl phosphate were added. The sub-samples were then incubated for 60 min at 37 °C, and then 1 mL 0.5 M $CaCl_2$ was added. Due to the high organic matter present in the soils, the solution was filtered first through Whatman #42 filter paper before 4 mL 0.5 M NaOH was added to complete the reaction. The concentration of phosphorus mineralised by phosphatase activity at each pH was measured colourmetrically.

2.6. Statistical analysis

Nutrient data were averaged within each sub-plot for each time interval. Repeated-measures, multivariate analysis of variance (MANOVA) was used to test for changes in nutrient adsorption with P fertilisation and over time (von Ende, 1993; Maxwell and Delaney, 2004) using a split-plot design. Repeated measures MANOVA treats time as an unique type of dependent variable and tests time as a correlated variable simultaneously with a unstructured variance-covariance matrix (von Ende, 1993). The repeated measures MANOVA was performed using the general linear model (GLM) procedure in SAS, version 9.1 (SAS Institute, Inc., Cary, NC). The split was for the sub-plot treatments and for the resin membrane data. For testing the within-subject effects of time, there are a number of tests used by SAS to contrast different time periods. The most robust and conservative test, Pillai's trace, was chosen to test the effects of time for all variables (Scheiner, 1993). Since only two unthinned and two thinned plots were sampled for foliar P in 2004, only these plots were chosen for the test of changes over time for this variable. As phosphatase activity was measured for one date, treatment effects were tested for with the analysis of variance procedure with GLM. Tukey's HSD test was used to compare means.

3. Results

3.1. Foliar P

Phosphorus fertilisation (HF treatment) significantly increased ($p = 0.003$) phyllode P concentration in 2004 and 2007 (Fig. 1). Thinning and time had no effect. There were no differences in the non-fertilised sub-plot treatments. Foliar P also increased in the fertilised treatment for other native understory woody species in 2004 (Scowcroft et al., 2008).

3.2. Hedley fractionation

Neither thinning nor herbicide had an effect on Hedley fractionation pools. Phosphorus fertilisation increased
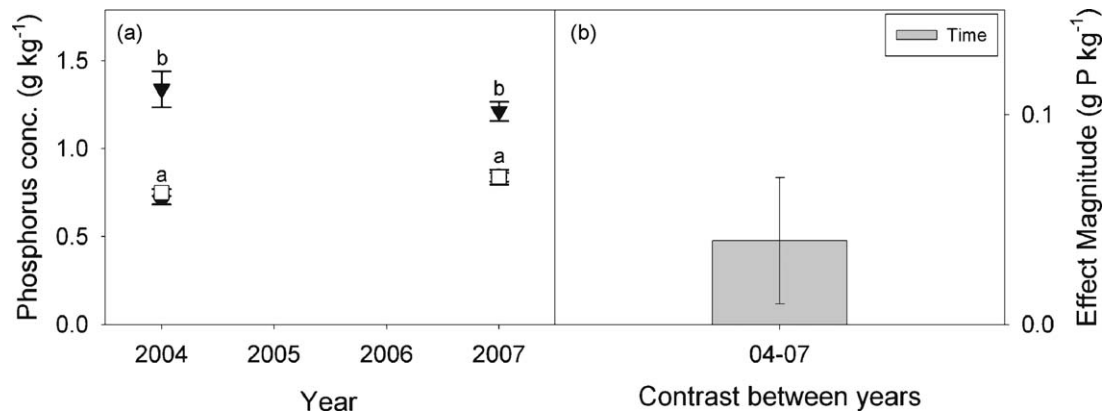
Fig. 1. Mean phyllode phosphorus concentrations (a) in February 2004 and September 2007 by sub-plot treatments of the control (○), herbicide (■), and herbicide + P fertilisation (▼). Different letters represent significant ($\alpha = 0.05$) treatment differences for that year only. (b) comparison of means (contrasts) between years. The overall mean difference (time) was plotted unless there was a significant interactions with the treatments. Standard error bars are shown ($n = 4$).

($p < 0.0001$) total P extracted by Hedley fractionation over the three years by an average of 370% (Fig. 2a). There was no difference in total extracted P between adjacent years, but 2007 was significantly greater ($p = 0.006$) than 2005 (Fig. 2b). Fertilisation had differing effects on individual P pools. For resin Pi, the HF treatment was greater ($p < 0.0001$) than the non-fertilised sub-plot treatments by a 960% (Fig. 3a). There were also significant differences between years ($p = 0.02$); the H and HF treatments in 2005 were less than the same treatments in 2006 and 2007 (Fig. 3b). Fertilisation significantly increased ($p < 0.0001$) the bicarbonate- and hydroxide- extractable Pi fractions by an average of 2900% and 1100%, respectively (Fig. 3c and e). There were no significant differences between years for these fractions (Fig. 3d and f). Fertilisation significantly increased ($p < 0.0001$) the hydrochloric acid-extractable Pi pool by 530% (Fig. 3g). There were significant time × sub-plot treatment interactions ($p = 0.03$) for this pool, as well. In the H and HF treatments, this pool increased between 2005 and 2006 but decreased in 2007 (Fig. 3h). The bicarbonate- and hydroxide-extractable Po pools showed complex time × sub-plot treatment interactions; however, neither pool declined over time and all treatments in 2007 were significantly greater than in previous years (Fig. 4b and d).

Fertilisation also shifted the relative proportions of total P in all fractions except for hydrochloric acid-extractable Pi (Fig. 5). Over the three-year study, the HF resin Pi fraction doubled ($p = 0.02$) from 3.0% to 6.9%. The proportion of bicarbonate- ($p < 0.0001$) and hydroxide- ($p < 0.0001$) extractable Pi fractions increased; from

0.8 to 5.1 % and from 20.7 to 52.8 % over three years, respectively (Fig. 5). Conversely, the proportion of bicarbonate- ($p = 0.002$) and hydroxide- ($p < 0.0001$) extractable Po fractions decreased; from 10.0% to 3.8 % and from 49.2% to 9.9% over three years, respectively (Fig. 5). These decreases in the proportion of organic P fractions were due solely to increases in the inorganic fractions rather than absolute decreases in the Po fractions.

3.3. Phosphatase activity

In 2007, fertilisation decreased acid phosphatase activity ($p = 0.03$) decreased from 12.3 to 10.4 μg P g^{-1} h^{-1}, and decreased alkaline phosphatase activity ($p = 0.001$) from 9.8 to 6.1 μg P g^{-1} h^{-1} (Fig. 6).

4. Discussion

The fertiliser treatment applied P at higher rates than is typically used in forestry. It was assumed at the beginning of the study that it would take several applications of P to overcome the very high P sorption capacity of the amorphous minerals. This assumption was based on the very high P application rates required for many agricultural soils in Hawaii. A koa fertilisation study on less P sorbing Oxisols and Ultisols found that koa seedlings did not respond until at least 300 kg P ha^{-1} was applied (Scowcroft and Silva, 2005). The soil P sorption capacity at the study site has not been tested. However, the P sorption isotherm of
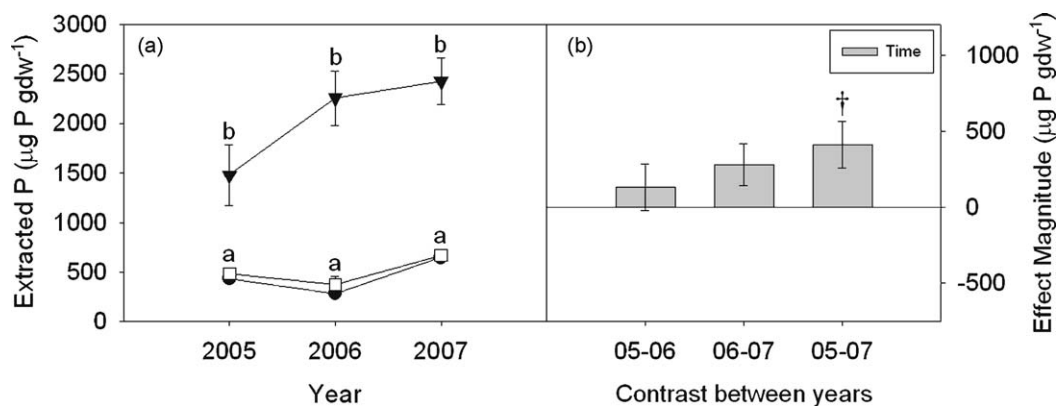

Fig. 2. Mean total Hedley extracted phosphorus at 5 cm depth (a) by sub-plot treatments of the control (○), herbicide (■), and herbicide + P fertilisation (▼) for March 2005, 2006, and 2007. Different letters represent significant ($\alpha = 0.05$) treatment differences for that year only. (b) comparison of means (contrasts) between years. The overall mean difference (time) was plotted unless there was a significant interaction with the treatments. To maintain an overall critical value of $\alpha = 0.05$, Bonferroni adjustment of 0.017 was used to test each contrast. Standard error bars are shown ($n = 8$; † significant at the 0.017 level).
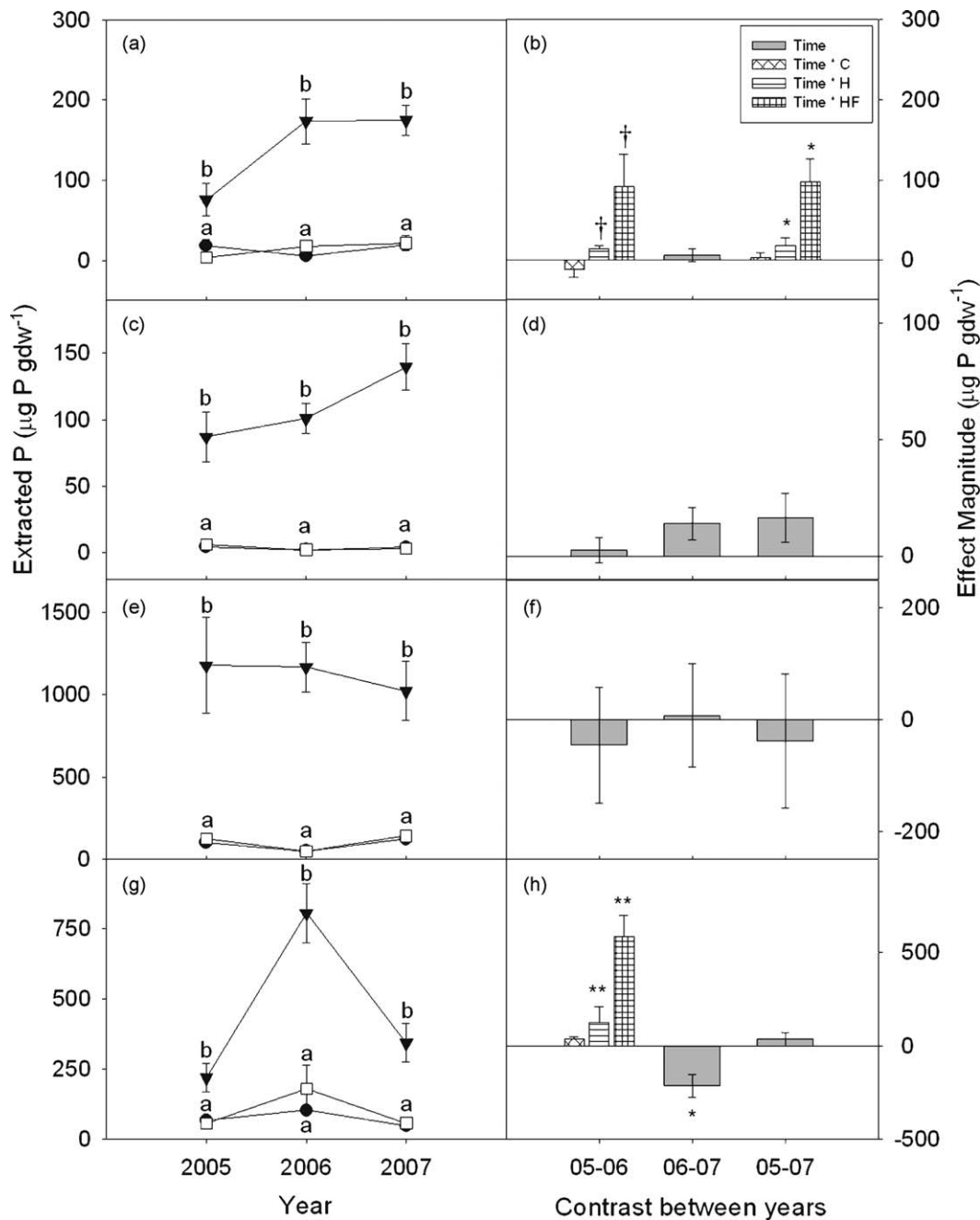
Fig. 3. Mean Hedley inorganic phosphorus (P) at 5 cm depth for resin (a), bicarbonate (c), sodium hydroxide (e), and hydrochloric acid (g) extractions by sub-plot treatments of the control (○), herbicide (■), and herbicide + P fertilisation (▼) for March 2005, 2006, and 2007. Different letters represent significant (α = 0.05) treatment differences for that year only. Comparison of means (contrasts) between years for resin (b), bicarbonate (d), sodium hydroxide (f), and hydrochloric acid (h) extractions. The overall mean difference (time) was plotted unless there was a significant interaction with the treatments. To maintain an overall critical value of α = 0.05, Bonferroni adjustment of 0.017 was used to test each contrast. Standard error bars are shown (n = 8). † significant at the 0.017 level, * significant at the 0.01 level.

a similar, uncultivated, Hydrudands (Kaiwiki series) showed that the P sorption capacity was 2138 mg P kg⁻¹ (Jackman, 1994). An estimate for increasing soil solution P by 10 ppm in the top 5 cm of the Kaiwiki series soil would require the application of 535 kg P ha⁻¹ (Hue et al., 2000). In comparison to P applications used in Hawaii, the level of fertilisation used in this study was not unduly excessive.

Scowcroft et al. (2007) showed that the increased growth of koa crop trees was associated with the almost doubling in P concentration in the canopy in 2004. Three years after the last P application, foliar P had not changed in the HF treatment, which indicates that koa continued to benefit from increased P availability. Phyllode P concentrations in the fertilised treatment

are near the maximum observed for koa in more naturally fertile but unmanaged koa stands (Ares and Fownes, 1999). The elevated live phyllode P concentrations corresponded to the elevated level of labile soil P that was measured in the resin Pi fraction through this study. This could indicate that the high foliar P was maintained by the uptake of elevated labile P, although it could also maintained through retranslocation and litter P cycling. Other data from this site showed that P retranslocation did not increase with fertilisation, while annual litterfall P doubled (Meason, unpublished data). Not only did it appeared to be no short term depletion of labile P after fertilisation, but the pool increased. The fertiliser effect of the resin Pi fraction reflected in situ measurements of labile P at the study site. A 45 day resin bag incubation in
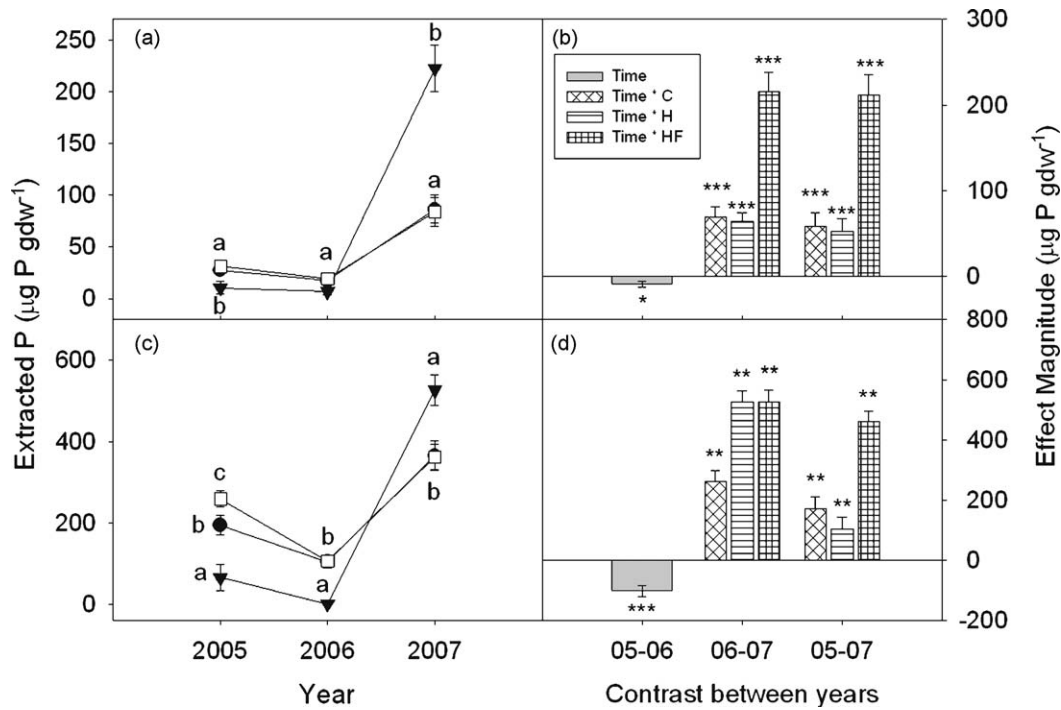
Fig. 4. Mean Hedley organic phosphorus (P) at 5 cm depth for bicarbonate (a), and sodium hydroxide (c) extractions by sub-plot treatments of the control (○), herbicide (■), and herbicide + P fertilisation (▼) for March 2005, 2006, and 2007. Different letters represent significant (α = 0.05) treatment differences for that year only. Comparison of means (contrasts) between years for bicarbonate (b) and sodium hydroxide (d) extractions. The overall mean difference (time) was plotted unless there was a significant interactions with the treatments. To maintain an overall critical value of α = 0.05, Bonferroni adjustment of 0.017 was used to test each contrast. Standard error bars are shown (n = 8). * significant at the 0.01 level, *** significant at the 0.0001 level.

May 2003 at 5 cm found labile P increased with fertilisation from 0.3 to 45.1 µg P bag^{-1} day^{-1} (Scowcroft et al., 2007). Measurements of labile P with ion exchange resin membranes between 2004 and 2007 at the same depth found that labile P for the fertilised treatment was consistently higher by over 3000% (Meason, unpublished data). Despite the increase in litterfall P return, it is unlikely that this was the primary source of the increase in labile P.

The elevated labile P was being readily replenished several years after the last P application and it is likely to remain elevated for at least for the next five years. The P pools measured in this study showed that it was not from pools typically assumed to be major P sources in forest soils. Research in forests on volcanic-ash

Andisols has indicated that there is a reliance on organic bicarbonate and hydroxide pools to cycle labile P (Thomas et al., 1999; Briceno et al., 2004). Previous studies in various Hawaiian forest ecosystems have indicated that organic and microbial P pools are the dominant factors regulating labile P (Zou et al., 1995; Binkley et al., 2000; Olander and Vitousek, 2004, 2005). The year-to-year fluctuations in the organic P pools in the non-fertilised treatments indicate the importance of these pools in koa forests. The organic pools were influenced by P fertilisation with a drop in the size of the pools in the first two years of the study. This could indicate that there was greater mineralisation of P from these
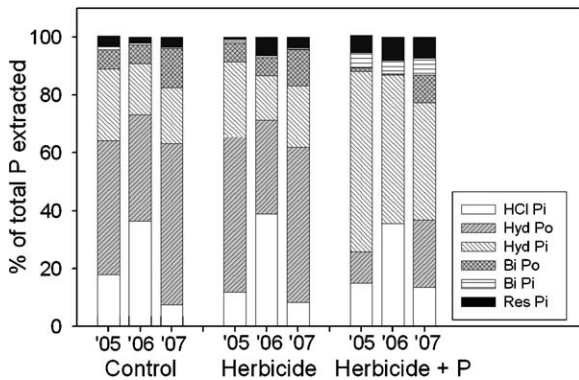

Fig. 5. The proportion of each soil phosphorus (P) pool at 5 cm depth in relation to the total P extracted by the Hedley fractionation by sub-plot treatment in March 2005, 2006 and 2007. Phosphorus pools are resin inorganic P (Res Pi), bicarbonate inorganic Pi (Bi Pi), bicarbonate organic P (Bi Po), sodium hydroxide inorganic P (Hyd Pi), sodium hydroxide organic P (Hyd Po), and hydrochloric acid inorganic P (HCl Pi).
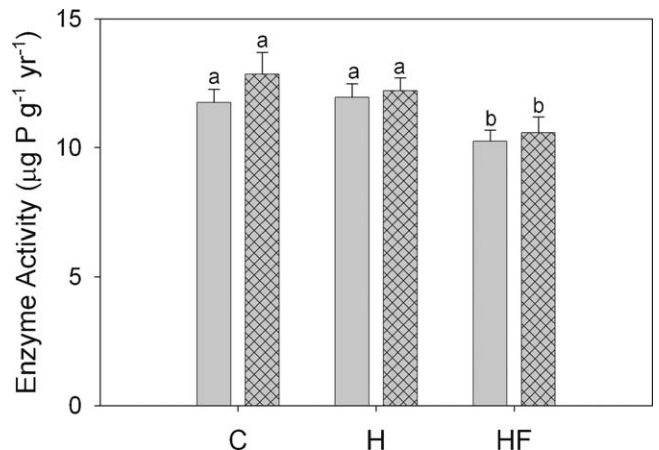

Fig. 6. Monophosphatase activity in March 2007 by sub-plot treatments; control (C), herbicide (H), and H + P fertiliser (HF). Plain bars represent phosphatase activity under acid conditions (pH 6.0) and hatched bars represent phosphatase activity under alkaline conditions (pH 11.0). Different letters represent significant (α = 0.05) treatment differences for that type of phosphatase activity. Stand error bars are shown (n = 8).

pools, which would contribute to the elevated P. However, the apparent increase in mineralisation was not large enough to explain the size of elevated labile P. Further, in 2007 the size of both organic pools was higher for fertilised treatment and soil phosphatase activity was less. Both indicate that the mineralisation of organic P was reduced, which could indicate that P demand was being met by other P pools. The data suggests that the organic pools were not the primary source of labile P after fertilisation.

For any of the P fractions in the HF treatment to be a potential source for maintaining elevated labile soil P, it must be of sufficient size and turnover at an adequate rate. All the inorganic P pools were increased with fertilisation over the length of the study. There was a large increase in the bicarbonate Pi pool, which is assumed to represent P that is readily available. However, the increase in this pool with fertilisation was only 106 μg P g^{-1}, which is unlikely to be large enough to supply labile P. The hydrochloric acid Pi pool increased by 530% with fertilisation, which could be from added P sorbed onto primary minerals or recalcitrant fertiliser granules. This pool is generally seen to represent calcium bound P that has a slow turnover (Cross and Schlesinger, 1995). Thus, it should have little impact on labile P during the length of the study. However, the large changes in this pool indicates that this "slow" pool played an important role of short term cycling of P for the fertilised treatment. The apparent rapid turnover of the hydrochloric acid - extractable pool could be driven P dynamics of recalcitrant fertiliser granules and the sorption and desorption of P. The hydrochloric acid Pi pool appeared to be important for short term P cycling for the unfertilised treatments too. This pool changed in size from year to year, especially for the herbicide treatment. As the soils less than 3000 years old, there would be a large source of P in the primary minerals. Thus, this pool may play a more dynamic role in P cycling for young soils.

There was also a large increase in the hydroxide-extractable Pi pool. This pool was a significant component of soil P in koa forests throughout Hawaii (Pearson and Vitousek, 2002). For the control treatment, the hydroxide Pi fraction was on average 21% of the total extracted P. With fertilisation, this pool increased to 53% of extracted P with an average size of 1100 μg P g^{-1} for any one year. The hydroxide Pi fraction was larger than the hydrochloric acid fraction and appeared to be more stable over the length of the study. Although there was a large increase in this pool with fertilisation, its size does not indicate its ability to supply P. The hydroxide-extractable Pi is commonly seen as a pool with slow P turnover due to the strong sorption of P to Al and Fe sites (Tiessen et al., 1984, Cross and Schlesinger, 1995). At best, this pool is generally seen to provide P at a slow rate of turnover (Cross and Schlesinger, 1995).

If P was able to be readily desorbed from this pool, it could be because of the high organic matter present. Organic matter can reduce P sorption or increase labile P in a number of ways (Guppy et al., 2005). One type of effect is that organic matter alters the surface charge of minerals by sorbing onto the surface and masking the charge properties of the underlying mineral colloids (Davis, 1982; Beckett and Le, 1990; Chorover and Sposito, 1995; Chorover et al., 2004). Soil carbon did not increase with fertilisation, but the organic matter already present might masked enough of the Al and Fe sorption sites to prevent some of the added P from being irreversibly sorbed. This type of sorption may not be possible unless there was a large increase in labile P from fertilisation. It is unknown if and how complexes between SOM and poorly crystalline allophanic minerals may affect charge properties of the soils at the study site or if such complexes could change the P sorption dynamics of the soil. Additional research is needed to better understand the P dynamics of the sodium hydroxide - extractable Pi pool and P cycling in after fertilisation as well as the duration of the fertiliser effect on labile P in koa forest soils.

Whatever the mechanism, this study does indicate that large applications of P fertiliser may not be required to increase labile P in koa forests with young Andisols.

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