Biogeochemistry **40:** 37–55, 1998.

The biogeochemistry of phosphorus after the first century of soil development on Rakata Island, Krakatau, Indonesia

WILLIAM H. SCHLESINGER[1,2,*], L.A. BRUIJNZEEL[3],
MARK B. BUSH[4], EMILY M. KLEIN[2], KIMBERLY A. MACE[1],
JANE A. RAIKES[2] & R.J. WHITTAKER[5]
[1]*Department of Botany, Duke University, Durham, N.C. 27708 USA;* [2]*Nicholas School of the Environment, Duke University;* [3]*Faculty of Earth Sciences, Vrije Universiteit, 1081 HV Amsterdam, The Netherlands;* [4]*Department of Biological Sciences, Florida Institute of Technology, Melbourne, Florida 32901 USA;* [5]*School of Geography, University of Oxford, Mansfield Road, Oxford, OX1 3TB, U.K. (* Author for correspondence: 919-660-7406 or schlesin@acpub.duke.edu)*

Accepted 8 July 1997

Key words: Krakatau, organic carbon, soil phosphorus, volcanic ash

Abstract. This study examined the accumulation of organic carbon (C) and fractions of soil phosphorus (P) in soils developing in volcanic ash deposited in the 1883 eruption of Krakatau. Organic C has accumulated at rates of 45 to 127 g/m^2/yr during 110 years of soil development, resulting in profiles with as much as 14 kgC/m^2. Most soil P is found in the HCl-extractable forms, representing apatite. A loss of HCl-extractable P from the surface horizons is associated with a marked accumulation of NaOH-extractable organic P bound to Al. A bioassay with hill rice suggests that P is limiting to plant growth in these soils, perhaps as a result of the rapid accumulation of P in organic forms.

Introduction

Studies of soil development have long relied on chronosequences – local comparisons of soils derived from similar parent materials but differing in age (Jenny 1941). Studies of new geomorphic surfaces, such as glacial deposits and volcanic ashfalls, show that biotic processes can rapidly affect nutrient availability and biogeochemical cycling during soil development. In a classic paper, Walker and Syers (1976) postulated a generalized sequence of expected changes in the forms and availability of soil phosphorus (P), based on their studies of several soil chronosequences in alluvium and dune sands up to 130,000 years old. Recent studies of soil development on volcanic lava flows on Hawaii provide a striking confirmation of the predicted trends – including a rapid increase in soil organic P with time (Crews et al. 1995).

Although most chronosequence studies examine soil development over l000s of years, rates of soil formation are often greatest during the early years of soil development and slow gradually thereafter (Bockheim 1980; Schlesinger 1990). For example, Singleton and Lavkulich (1987) found that over 99% of Ca-bound P, largely in carbonates, was lost within 500 years of soil development in dune sands on Vancouver Island, British Columbia. Crocker and Dickson (1957) found that nitrogen (N) accumulated at a rate of 40 kg/ha/yr during the first 50 years of soil development on glacial deposits in Alaska, but the accumulation slowed to less than half that rate during the next 100 years.

On August 27, 1883, the island of Krakatau, west of Java (Indonesia), exploded in a catastrophic volcanic eruption. The steep, concave northwest coastline of Rakata, a present-day remnant of Krakatau, outlines a portion of the submarine caldera (Thornton 1996). In this paper, we report on 110 years of soil development on Rakata, using a toposequence of sites extending from near its summit (735 m) eastward to a site near the coast (100 m). The parent material of soil formation is dominated by the pyroclastic ashfall of 1883, with no convincing evidence for additions of ash from Anak Krakatau in subsequent years (Whittaker et al. 1992).

Whittaker et al. (1989) described the historical recolonization of vegetation on Rakata, which has led to a well-developed forest in today’s tropical climate. Mean annual temperature is about 27 °C, and regional rainfall ranges from 2500 to 3000 mm/yr (Shinagawa et al. 1986a; Hafkenscheid 1994). Hardjowigeno (1992) described the basic soil characteristics – mineralogy, texture, acidity, and exchangeable base cations – on Rakata, and Shinagawa et al. (1986b, 1992) classified the soils on Rakata as Andeptic Troporthents. Our work focuses on the accumulation of organic P and C during early soil development. We supplement our descriptive analyses of soil characteristics with a greenhouse bioassay of the nutrient limitations for plant growth in soils collected at 100-m and 720-m elevations.

Methods

Soils were collected during a 1992 expedition to Rakata by Bush and Whittaker. A 1.5-km sampling transect containing 4 sites extended from a site at 720-m elevation near the summit of Rakata to the east coast (l00-m elevation) (see Figure 1 in Bush et al. 1992). Sites at 100- 155-, 480-m elevations were located in closed forest of 30 to 35m height dominated by *Neonauclea calycina*, including *Ficus pubinervis*, *Dysoxylum gaudichaudianum*, *Terminalia catappa*, and *Crypteronia paniculata* as secondary associates at the lower elevations (Whittaker et al. 1989; Bush et al. 1992). The 720-m elevation site was in a shrub forest dominated by *Schefflera polybotrya*, with *Saurauia nudiflora, Vernonia arborea, Cyrtandra sulcata, Ficus ribes*, and an occasional *Neonauclea calycina* as secondary associates. The canopy is open and about 12 m in height.

In most areas of Rakata, the volcanic ash deposits are deeply incised by the channels of ephemeral streams. Soils were collected from topographic "ridge" (i.e., interfluve) locations, avoiding gullies. At each site, the surface litter was removed, a soil pit was excavated until unaltered (whitish) 1883 ash was encountered, and samples were obtained from 4 to 5 visible horizons comprising the entire soil profile. Samples were air-dried in the field and shipped to Durham, North Carolina, where they were kept refrigerated until analysis.

Subsamples of each soil were subjected to sequential P fractionation procedures described by Tiessen and Moir (1993) to isolate P held in a variety of inorganic and organic and bio-available and unavailable forms. These samples were first passed through a 2-mm sieve, and 0.5 g of each soil was placed in a 50-ml centrifuge tube containing 30 mls of distilled water and a 0.25-cm^2 section of an anion-exchange membrane (Ionics 204-U-386, Ionics, Watertown, MA; Abrams & Jarrell 1992) saturated with Cl. After being shaken for 16 hr, the membrane was removed, and PO_4 eluted from it by 1M HCl (i.e., resin-extractable P) was determined on a Traacs 800 autoanalyzer. The soil remaining in the tube was recovered by centrifugation (3800 rpm for 10 min.) and filtration (Whatman 42), and used in the remaining extractions, as described by Tiessen and Moir (1993). These include HCO_3-extractable (plant available-P), NaOH-extractable (P bound to Fe and Al minerals), HCl-extractable (Ca-bound P), and residual forms of P. On each sample, the analysis was performed sequentially; at the end of each step, the remaining soil was recovered by centrifugation and filtration, and used in the next extraction. All solutions were analyzed on the Traacs autoanalyzer with standards mixed in the relevant extractant solutions to minimize matrix effects. A manual analysis of PO_4 in the NaOH extract of 7 soils using the Murphy & Riley (1962) method showed a good comparison (slope = 1.03; r^2 = 0.987) with the autoanalyzer values.

Persulfate digestions of each of these extractant solutions were used to determine P held in organic forms (i.e., PO_4 in digested sample minus PO_4 in undigested sample; Tiessen & Moir 1993). Recovery of organic P from standards mixed with fructose-6 phosphate was 85–95% (r^2 = 0.998). An independent set of 36 samples was subjected only to the final step of the sequential phosphorus fractionation. Values of total P, calculated by summing the individual fractions determined following Tiessen and Moir (1993), were an average of 3.5% less than the independent analysis of total P on these samples.

Subsamples analyzed for organic C and total N were first ground in a shatterbox (SPEX Industries Model 8500) and then analyzed on a Perkin Elmer Model 2400 CHN analyzer. Six samples were also analyzed for δ^{15}N on the VG Isogas Mass Spectrometer facility at Duke University. We also measured P adsorption capacity of each soil, expressed as the % P removed from 25 ml of a solution containing 25 mg of P (as KH_2PO_4) shaken with 5 g of soil (Blakemore 1984).

Extractions of ground soils with 2M KCl, Na pyrophosphate, and acid ammonium oxalate were used to quantify exchangeable, organic, and non-crystalline (amorphous) forms (respectively) of Fe and Al in two 0.5-g subsamples of each soil (McKeague et al. 1971). Magnetite was removed before analysis (Walker 1983), and the oxalate extractions were maintained in the dark throughout the procedure (McKeague & Day 1966). These analyses were not performed sequentially. A Direct Current Plasma Emission Spectrometer (Spectraspan 7; Applied Research Laboratories) was used to measure Fe, Al, and Si in each of these solutions, as well as P in the oxalate solution, following methods modified after Klein et al. (1991). Samples were calibrated to synthetic standards made from 1000 ppm single-element stock solutions added to each matrix solution to create standards in appropriate concentrations for each extraction.

Soil bioassay

Soils used in the greenhouse study were collected from 0–5 cm depth at ridge locations at 110 m and 720 m elevations in August 1992. These soils were air dried in the field and shipped to Vrije University in Amsterdam. Pumice gravel was removed and the remaining soil from each site was mixed and distributed into 20 0.5-liter pots, each containing about 400 g of soil. Five additional pots were filled with a commercial potting medium consisting of peat.

Seven pregerminated seeds of hill rice (*Oryza sativa*) were planted in each pot, and seedlings were thinned to five as soon as the shoots emerged. Three fertilizer treatments (N, P, and N+P) were added to five replicate pots of each soil. Nitrogen was added as 485 mg $NaNO_3$ and phosphorus as 180 mg NaH_2PO_4 per pot – both administered in 50 ml of distilled water. The total of 45 pots was laid out randomly in nine rows, which were re-randomized each week. The plants were watered with demineralized water and grown under a daily regime of l2 hours of artificial light. Temperature and relative humidity were between 15 and 28 °C and 70 and 90%, respectively, resembling conditions of the humid tropics. Aboveground biomass (leaves) and roots (except for plants grown in peat) were harvested after six weeks and weighed to the nearest mg.

Results

Each soil profile shows a strong accumulation of C (8.2–20%) in the surface horizon, with organic C declining monotonically to $<1\%$ with increasing depth (Figure 1). The thickness of the surface organic accumulation declines with increasing elevation; soil C contents $>1\%$ extended to 57-cm depth at the 100-m site, versus 12 cm at 720-m elevation. Among all samples, organic N is strongly correlated to organic C ($r^2 = 0.99$). Carbon-to-nitrogen ratios range between 12–16 in the surface horizons, declining to 10 in the deepest layers sampled in each profile. We were unable to measure bulk density in the field, so we used Hafkenscheid's (1994) value of 0.65 g/cm^3 for the surface horizon (0–6 cm) and 0.8 g/cm^3 for all lower horizons to estimate the total profile contents of C and organic P. Total C content ranges from 4.9 kg/m^2 at 720-m elevation to 14.0 kgC/m^2 at 480-m elevation, indicating rates of accumulation of 45–127 gC/m^2/yr during 110 years of soil development since the 1883 eruption.

Contents of pyrophosphate-extractable Al and Fe (Al_p and Fe_p, respectively) and oxalate-extractable forms (Al_{ox}, Fe_{ox} and Si_{ox}) tend to increase with elevation (Table 1). In each soil the maximum value for Al_p and Fe_p is found at a mid-profile depth, suggestive of podzolization; the highest value for the ratio Al_p/Al_{ox} is found at 3–6 cm depth in the profile at 720-m elevation. Greater quantities of pyrophosphate-extractable (organic) Al and Fe at higher elevation may indicate more rapid podzolization under the cool moist conditions at these sites on Rakata.

From a worldwide survey of soils, Parfitt and Kimble (1989) suggested that the ratio of Al to Si extracted from amorphous minerals can be used to estimate the content of allophane in soils. Among the samples from Rakata, Al_{ox}-Al_p is highly correlated to Si_{ox} (Figure 2; ratio Al/Si = 1.73), but even the highest value for Si_{ox} (17–20 cm depth at 480-m elevation) would indicate an allophane content of only 2.0% (Parfitt & Kimble 1989). Shoji et al. (1993a) suggest that a content $>0.4\%$ of the sum [$\%Al_{ox}$ + 1/2 $\%Fe_{ox}$] can be used as an index of Andic soil horizons. In the samples from Rakata, [$\%Al_{ox}$ + 1/2 $\%Fe_{ox}$] is $>0.4\%$ in all samples collected at 480 and 720-m elevations, but at the other sites most values are $<0.4\%$. The P-adsorption capacity of these soils is not well correlated to [Al_{ox} + 1/2 Fe_{ox}] ($r^2 = 0.29$), and our values for P adsorption, ranging from 15–50%, are consistent with the low levels of amorphous Al and Fe in these soils (Shoji et al. 1996). Based on these

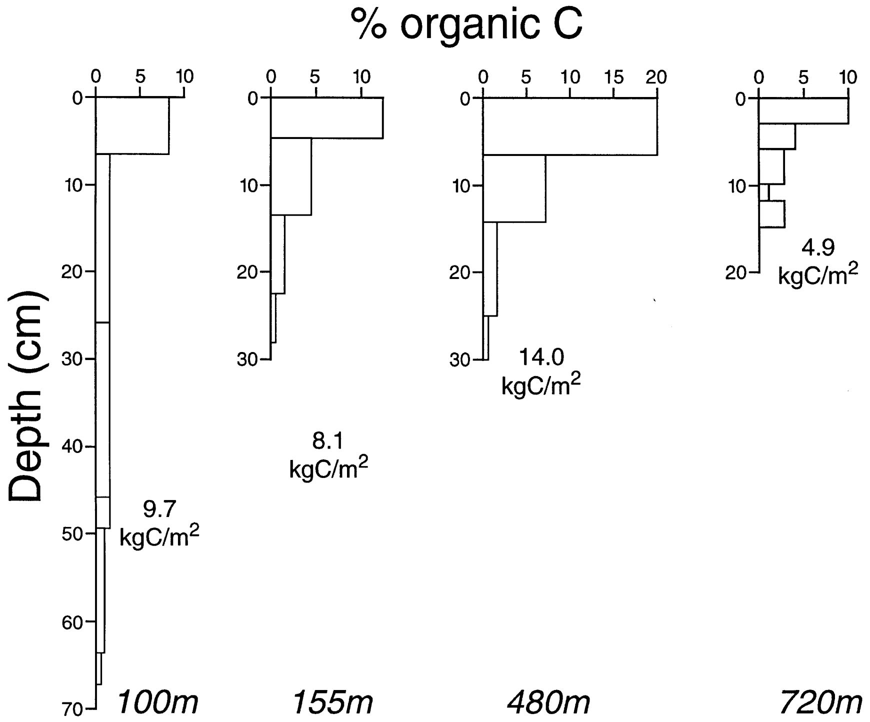

Figure 1. Total profile content and depth distribution of organic carbon in four soil profiles on Rakata.

properties, none of these soils meet the minimum criteria of a vitric Andosol (Shoji et al. 1996).

The total phosphorus content (g/m^2) difers widely among the 4 soil profiles, as a result of differences in the depth of sampling at each site (Figure 3a). However, the total phosphorus content in the 0–30 cm layer of the profiles at 100-, 155-, and 480-m elevations varies within a narrow range (117–135 g/m^2), as does total P in the 0–15 cm layer of all 4 profiles (range 51 to 71 g/m^2). The HCl-extractable P in the lowest layer of each profile, which is indicative of the P mineralogy of the original ash is also very similar among the profiles from 155 to 720 m elevation (232 to 257 μg/g), but somewhat higher in the profile at 100 m (384 μg/g; Table 2). The values in the higher elevation sites are similar to the average content of total P measured in recent ash deposits on the adjacent islands of Panjang and Sertung (250 μg/g; unpublished data).

Among the 4 soil profiles, total soil P ranges from 600–700 μg/g in the surface horizons, declining to 450–550 μg/g at the bottom of the sampled profile (Table 2; Figure 3). As in many Entisols, the largest component of

Table 1. Chemical extraction of Rakata soils. All values are μg/g unless indicated.

Site	Horizon (cm)	Al_e	Al_p	Al_o	Fe_e	Fe_p	Fe_o	Si_o	Al_p/Al_o	[%Al_o + 1/2 %Fe_o]	(Al_o − Al_p)/Si_o
100 m	0–3	2.2	31	1500	0	0	1970	368	0.02	0.248	3.99
	10–12	6.6	55	1810	4.7	26	2906	527	0.03	0.326	3.33
	40–42	0	0	1644	4.9	0	2370	58	0	0.283	2.81
	57–60	7.7	0	1515	0	0	3017	573	0	0.302	2.64
	67	3.5	0	1556	4.3	0	2704	614	0	0.291	2.53
155 m	0–3	6.7	33	1583	18.0	70	2445	447	0.02	0.281	3.47
	6–10	7.1	594	2374	19.3	305	5844	804	0.25	0.530	2.21
	17–20	9.2	2	1285	16.8	173	2282	435	0.0014	0.243	2.95
	25–28	6.8	0	754	19.3	0	1767	320	0	0.164	2.36
480 m	0–3	12.9	975	3354	17.4	568	3812	479	0.29	0.526	4.97
	10–12	6.0	1083	5262	16.8	598	5077	1902	0.21	0.780	2.19
	17–20	6.7	81	3215	16.5	0	3921	2614	0.025	0.518	1.19
	30	6.1	4	5064	14.4	0	3031	1986	0.0010	0.658	2.54
720 m	0–3	11.3	617	2895	5.3	523	3905	485	0.21	0.485	4.69
	3–6	11.9	1998	3928	0	1463	4983	872	0.51	0.642	2.22
	6–10	16.9	2165	4363	5.8	1499	4107	1073	0.50	0.642	2.05
	10–12	9.1	504	3485	4.5	240	2977	1259	0.15	0.497	2.37
	12–15	22.2	2286	5185	6.1	1518	4071	1505	0.44	0.722	1.93

P is held in the 1M HCl-extractable fraction (Cross & Schlesinger 1995). In carbonate-free soils, this fraction is usually taken to represent P derived from primary apatite. The decline in P content with depth is due largely to an accumulation of organic P in the surface horizons, where the largest proportion of organic P (55±3.4% S.D.) was isolated in the NaOH fraction. Organic P extracted with NaOH was strongly correlated to soil organic C (Figure 4). Organic P always greatly exceeded inorganic P in the NaOH fraction, which is generally assumed to contain P bound to iron and aluminum minerals. Among all samples, total organic-P is negatively correlated to inorganic P extracted with 1M HCl (Figure 5), suggesting that the weathering of apatite mobilizes P that is subsequently captured and retained in organic forms.

Total P extracted with the acid ammonium oxalate solution, which contains both P bound to organic matter and P bound directly to amorphous minerals, is well correlated to organic P extracted with NaOH (Figure 6). Organic-P extracted with NaOH is better correlated with Al_p or Fe_p (r^2 for both = 0.35) than with Al_{ox} or Fe_{ox} (r^2 = 0.03 and 0.13, respectively). The P-adsorption

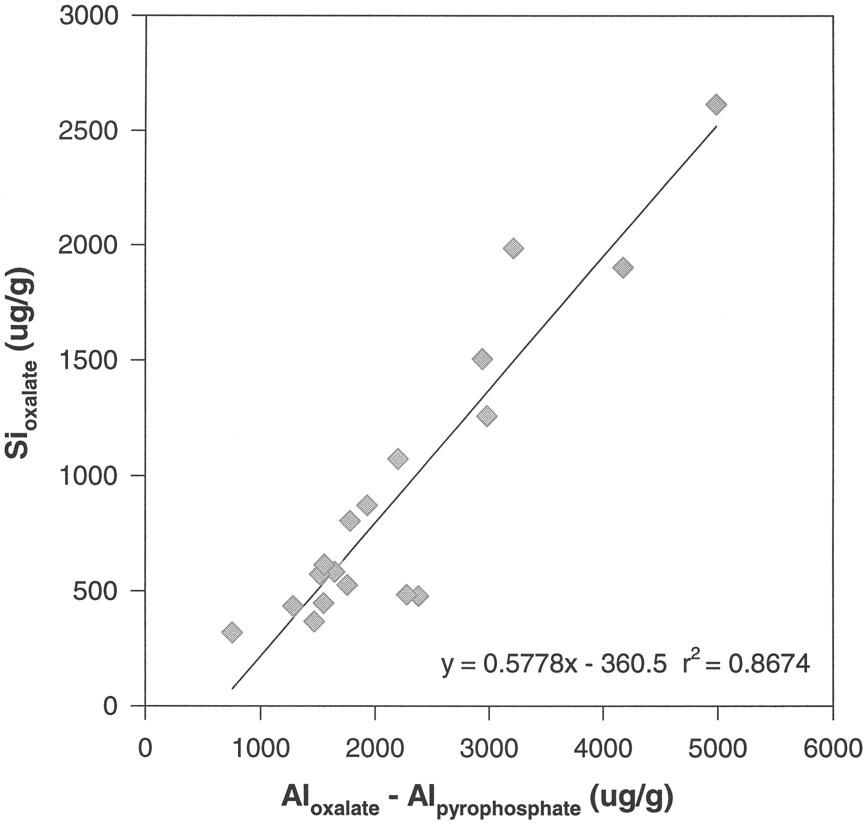

Figure 2. Depth distribution of total phosphorus, HCl-extractable phosphorus and total organic phosphorus, following the methods of Tiessen and Moir (1993), in the soils on Rakata.

capacity of Rakata soils is correlated to the total of Al_p and Fe_p (Figure 7), suggesting that it derives from metal-humic complexes.

In the soil profiles at l55 and 480-m elevations, HCl-extractable P tends to increase with depth, suggesting that weathering is concentrated in the surface horizons, with unaltered ash remaining at depth (Table 2; Figure 3). We estimated the total loss of HCl-extractable P from the upper soil profile by assuming that soil development began in a uniform layer of ash with a bulk density of 0.8 g/cm^3 and an HCl-extractable P content equal to that found at the lowest depth sampled at each site. The loss of HCl-P from the soil profile appears to be associated with the accumulation of total organic P, although the regression, with only 4 points, is not significant (Figure 8). The accumulation of organic-P exceeds the loss of HCl-P, suggesting that other sources of P, including plant uptake from lower soil depths, are likely to contribute to the accumulation of organic P during soil development.

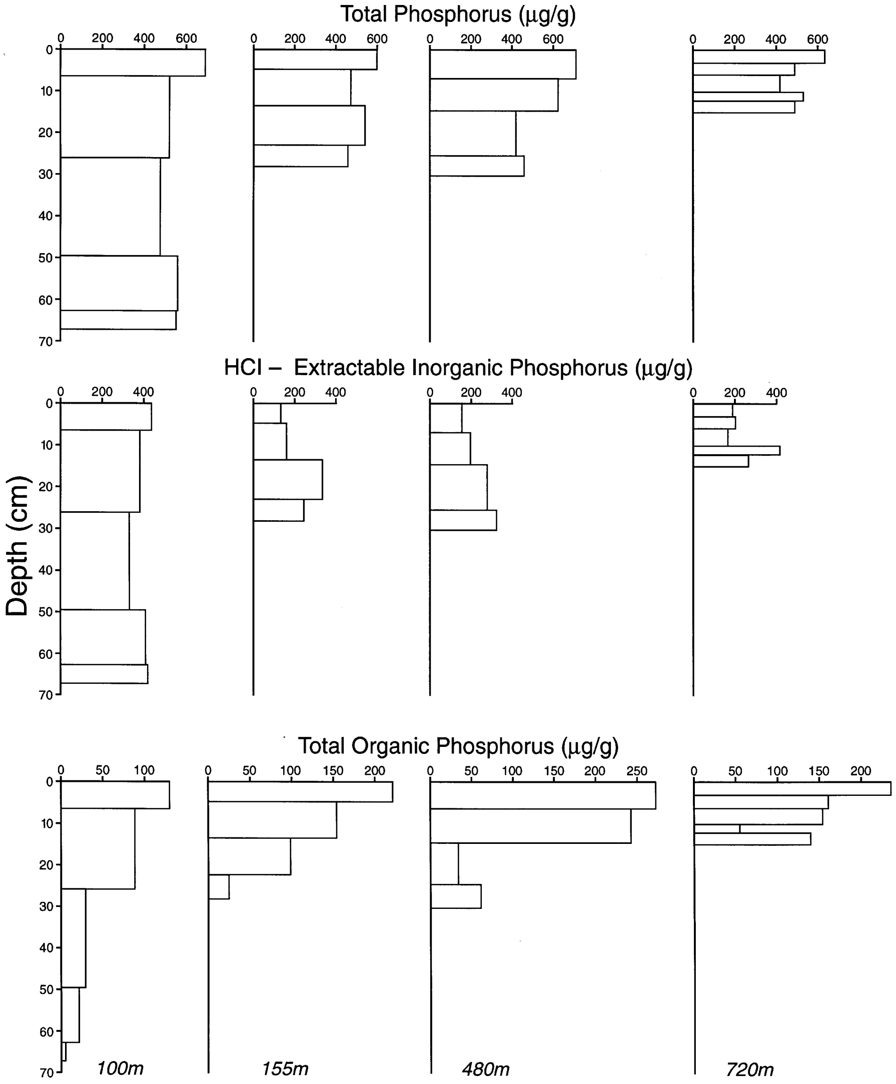

Figure 3. Si extracted by ammonium oxalate solution as a function of the content of Al derived from amorphous minerals (Al_o-Al_p) in 18 samples from the 4 profiles on Rakata.

Soil bioassay

Mean leaf and root mass and shoot/root ratios for respective treatments are given in Table 3. There were no differences in leaf or root biomass between the two control soils, while the leaf mass of the plants grown in peat was about 2.6 times greater. Leaf mass increased significantly by fertilization with P (both

Table 2. Phosphorus fractionation (method of Tiessen & Moir (1993)). All values are μg/g unless indicated.

Site	Horizon (cm)	Resin P	Bicarb P (P_o & P_i)	NaOH P P_o	NaOH P_i	HCl P_i	Con. HCl (P_o & P_i)	Residual P	Total P_o	Total P_i	P total
100 m	0–3	41.9	36.9	69.9	41.1	396.0	80.6	41.8	129.4	578.8	708.2
	10–12	11.5	15.6	64.12	40.4	341.2	59.5	40.4	92.9	479.8	572.7
	40–42	9.7	12.9	3.72	65.6	308.9	44.8	40.0	29.6	456.0	485.6
	57–60	22.8	14.7	8.28	73.4	373.6	49.2	33.8	24.6	551.2	575.8
	67	38.1	16.9	0	78.0	383.8	39.9	20.4	4.8	566.3	571.1
155 m	0–3	93.6	50.6	121.0	60.7	76.4	135.9	61.0	222.7	376.5	599.2
	6–10	12.2	33.1	103.5	69.3	117.7	73.8	56.8	156.2	310.2	466.4
	17–20	24.0	29.2	81.7	48.2	303.7	30.2	25.3	101.5	440.8	542.3
	25–28	77.6	40.4	4.8	37.7	257.8	25.7	12.3	22.3	434.0	456.3
480 m	0–3	99.0	79.4	147.6	57.3	80.3	176.4	71.0	274.1	436.8	710.9
	10–12	13.5	38.3	151.1	51.6	129.7	135.8	122.4	243.2	399.2	642.4
	17–20	1.3	5.1	47.4	35.7	270.1	63.1	32.0	61.7	393.0	454.7
	30	1.5	19.0	20.5	50.9	237.5	46.5	37.1	35.0	378.0	413.0
720 m	0–3	32.5	76.3	143.7	72.2	142.9	97.6	63.3	236.4	392.1	628.5
	3–6	6.6	37.5	119.7	58.7	161.8	47.8	53.3	159.5	325.9	485.4
	6–10	3.0	28.4	111.3	52.7	123.0	52.7	42.4	152.5	261.0	413.5
	10–12	1.1	10.8	39.0	38.3	385.9	31.3	24.8	53.6	477.4	531.0
	12–15	1.2	23.0	104.2	44.0	231.7	43.5	34.4	141.9	340.1	482.0

as P and N+P) in the lowland soils ($P < 0.01$ and $P < 0.05$, respectively), and with N+P added to the montane soil ($P < 0.05$). The addition of P (as P and N+P) to the montane soil caused a significantly lower root mass ($P < 0.01$).

Discussion

Following Shinagawa et al. (1992), we believe the soils of Rakata are best classified as Andeptic Troporthents. Although they have a number of properties suggestive of allophane mineralogy, they do not now contain the minimum percentage of amorphous Al and Fe minerals for recognition as Andic soils (Shoji et al. 1993a). One can easily envision that allophane will eventually accumulate in these profiles, which are forming in volcanic ash, at near-neutral pH, and under a climatic regime with >2500 mm/yr of precipitation. Shoji et al. (1993b) found Andic soil properties to have developed within a few centuries in volcanic deposits in Japan, where the mean annual temperature ranges from 5.4 to 13.4 °C and precipitation ranges from 1030 to 1860 mm/yr. Higher quantities of Al_{ox} and Fe_{ox} in the samples from 480- and

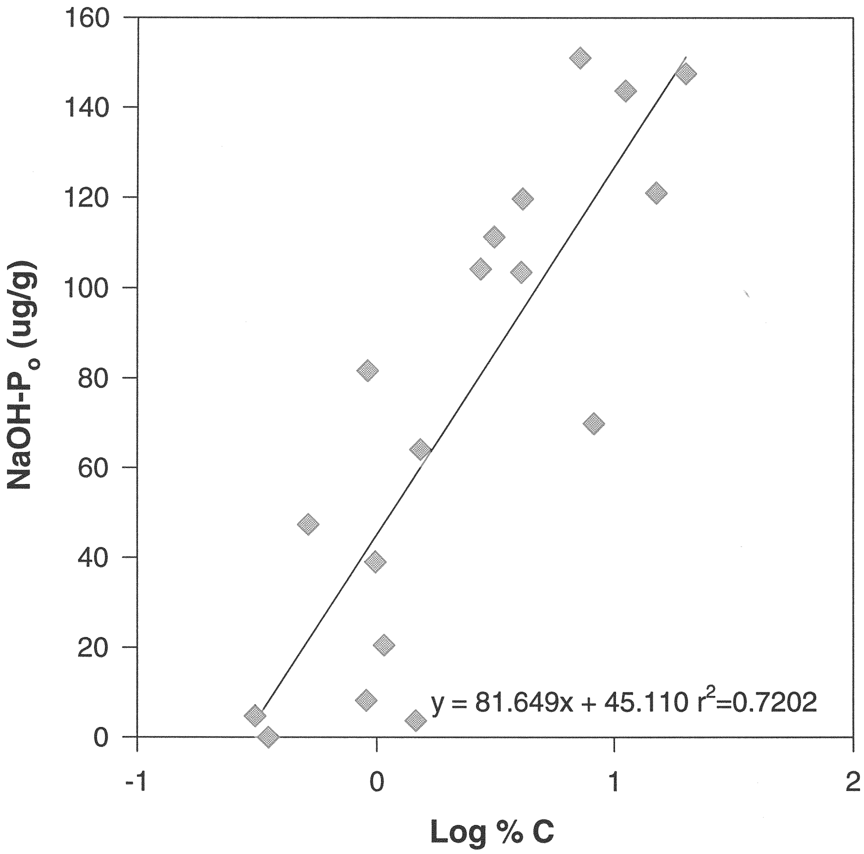

Figure 4. Correlation between organic-phosphorus (extractable with NaOH) and the logarithm of organic carbon in 18 soil samples from Rakata. The regression is significant ($P < 0.05$).

720-m elevations suggest that allophane will first appear in the soil profiles at higher elevations on Rakata.

The soil profiles included in this study appear to have developed in stable interfluve positions, but given the steep topography on Rakata, we cannot dismiss the possibility that these profiles have been affected by lateral transport, slumps, and erosion of the original ashfall deposits. Despite their youth, some montane soils on Rakata have organic C contents that exceed the mean content found in well-developed tropical soils globally (10.4 kgC/m^2; Schlesinger 1977) and in 162 profiles from moist tropical forests (11.5 kgC/m^2; Post et al. 1982). Volcanic soils often contain large accumulations of organic matter, but the rates of accumulation of 45 to 127 gC/m^2/yr on Rakata are well in excess of the accumulation rates observed in other young volcanic soils developing on lava and ash (e.g., Tezuka 1961; Sollins et al.

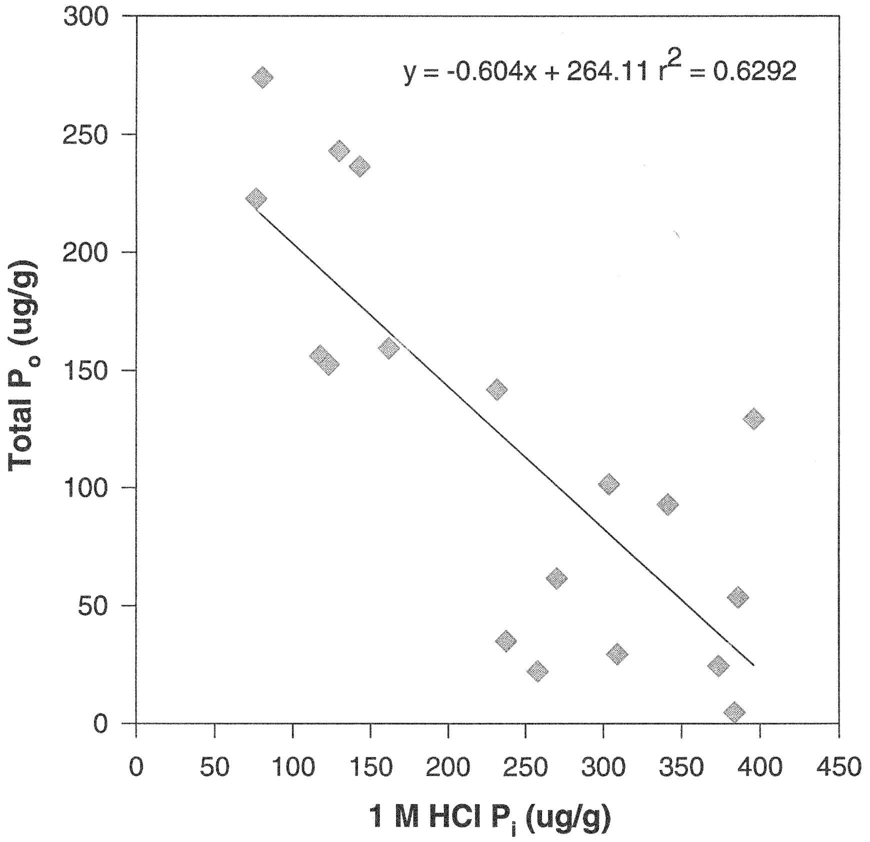

Figure 5. Correlation between total organic phosphorus and inorganic phosphorus extractable with 1M HCl for 18 soil samples from Rakata. The regression is significant ($P < 0.05$).

1983; Vitousek et al. 1983), and they far exceed the long-term mean rate observed in world soils (2.4 gC/m^2/yr, Schlesinger 1990).

The accumulation of organic N in the soil profiles on Rakata implies a minimum N input of 30 to 85 kg/ha/yr. For a site with similarly high rainfall, Bruijnzeel (1989) reported an atmospheric deposition of about 15 kgN/ha/yr in a forest plantation in central Java. Assuming that this input is typical of the humid western part of the Indonesian archipelago, a large amount of N in these soils must also derive from biological fixation. Our six analyses of the organic N in surface soils on Rakata show δ^{15}N values ranging from -0.7 to -2.2‰, only slightly depleted from the global mean value for the atmosphere and indicative of N-fixation as a major source of nitrogen. In contrast, the organic matter in most forest soils shows positive values for δ^{15}N, due to depletion of the light isotope during microbial mineralization

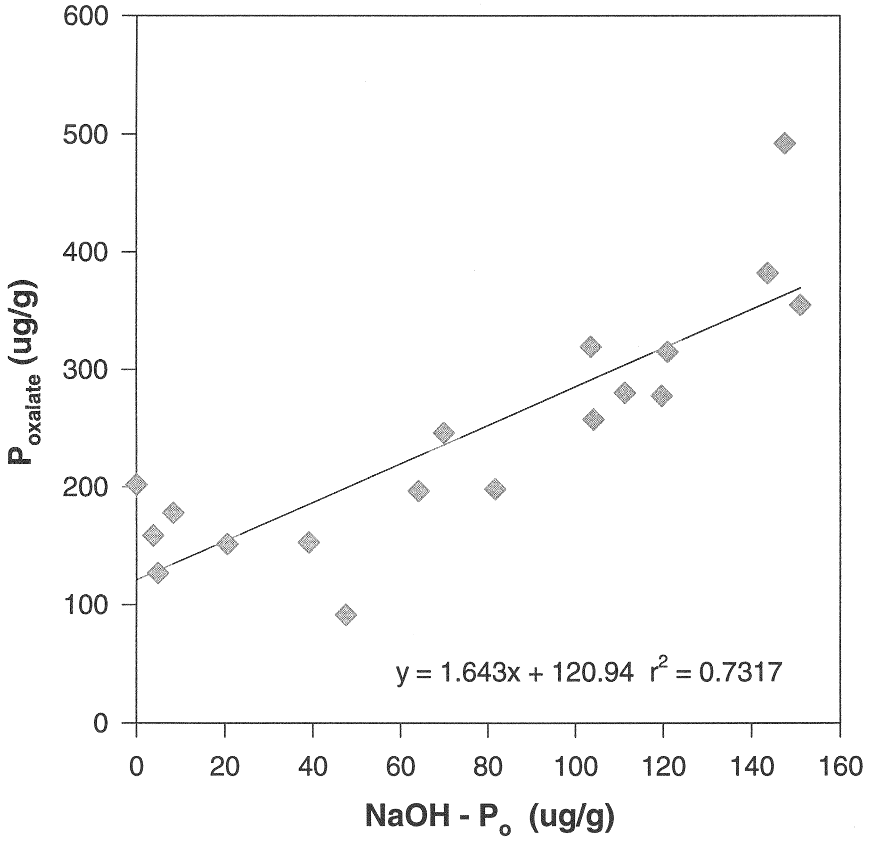

Figure 6. Relationship between P, extractable with ammonium oxalate, and NaOH-extractable organic phosphorus for 18 soil samples from Rakata. The regression is significant ($P < 0.05$).

and denitrification (Schlesinger 1997; Garten & Van Miegroet 1994; Piccolo et al. 1996).

Whittaker et al. (1989) list a large selection of Leguminosae in the current flora of the Krakatau island group, but of the legumes recorded between 1883 and 1993, all are primarily sea-dispersed stand-line or near-coastal species. Of the several diplochorous species that have spread inland, none occurs higher than about 100 m elevation on Rakata. We have no measures of asymbiotic N fixation in the soils on Rakata, but Ernst (1908) quotes an 1886 report by Treub that the surface of Rakata was covered with a gelatinous layer of blue-green algae. Although N inputs by asymbiotic bacteria typically range from 1 to 5 kg/ha/yr (Boring et al. 1988), inputs of over 100 kg/ha/yr have been reported in some barren desert soils (Rychert et al. 1978).

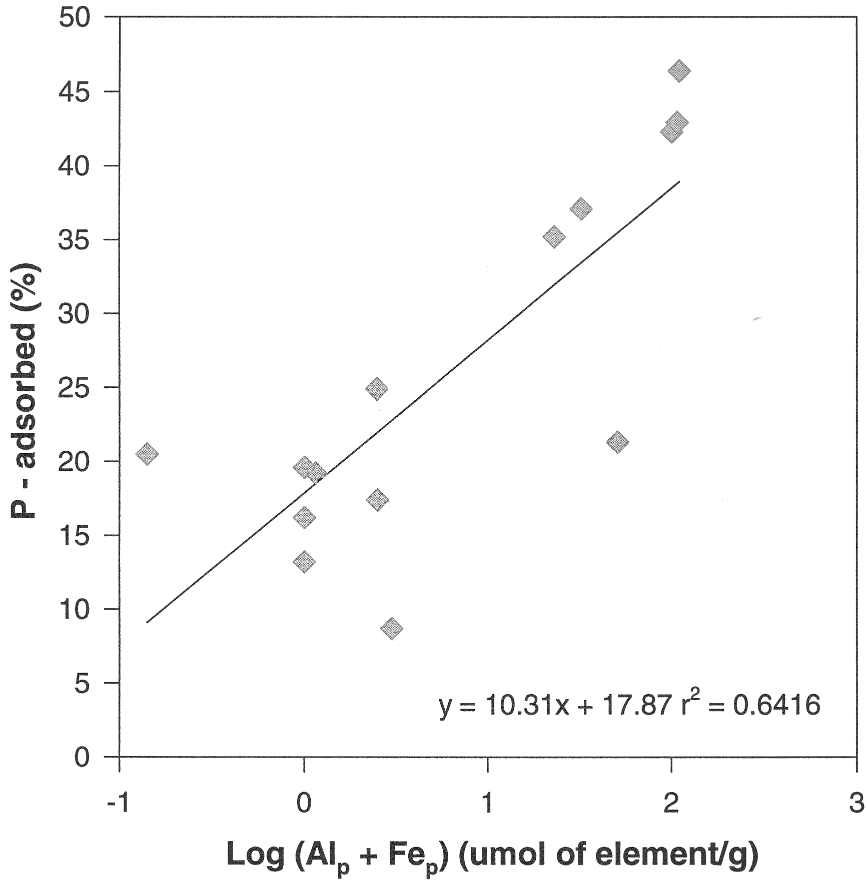

Figure 7. The P-adsorption capacity (following Blakemore 1984) of 18 soils from Rakata as a function of the logarithm of the total amount of Al and Fe extractable with pyrophosphate solution. The regression is significant ($P < 0.05$).

High P adsorption is associated with many volcanic soils that have significant Al-humus complexes or allophane content (Wada 1985; Shoji et al. 1993a). The high content of NaOH-extractable organic P would seem to suggest binding to Fe and Al minerals; however, oxalate-extractable P is poorly correlated to oxalate-extractable (amorphous) forms of Al and Fe (r^2 = 0.13). The P-adsorption capacity in Rakata soils, ranging from 15 to 50% of added P, was better correlated to the content of Al and Fe extractable in pyrophosphate – i.e., metallo-humic compounds (Figure 7) than to oxalate-extractable forms. Unfortunately, the pyrophosphate extraction is also known to remove Al from amorphous minerals, especially when they are coated with organic matter (Kaiser & Kech 1996). Both oxalate-extractable P and

Table 3. Leaf and root mass (g) and shoot/root ratios of hill rice seedlings grown for six weeks in lowland soil (LS), montane soil (MS), or commercial potting medium (Peat) with or without fertilizer addition. Values are means (±S.D.) of five pots, each containing 5 seedlings. Asterisks indicate values that are significantly different from the respective control samples at $^{*} = P < 0.05$ and $^{**} = P < 0.01$.

Treatment	Leaf mass (g)	Root mass (g)	Shoot/root ratio
LS control	0.50 ± 0.13	0.16 ± 0.06	3.2 ± 0.5
LS+N	0.52 ± 0.08	0.15 ± 0.02	3.4 ± 0.2
LS+P	0.82 ± 0.05**	0.17 ± 0.02	4.8 ± 0.5**
LS+NP	0.89 ± 0.16*	0.19 ± 0.05	4.8 ± 0.7
MS control	0.48 ± 0.05	0.16 ± 0.02	2.9 ± 0.3
MS+N	0.53 ± 0.06	0.16 ± 0.01	3.3± 0.3
MS+P	0.57 ± 0.05	0.08 ± 0.02**	7.6 ± 0.9**
MS+NP	0.62 ± 0.12*	0.08 ± 0.01**	7.9 ± 0.8**
Peat	1.29 ± 0.02	nd	nd

NaOH-extractable organic P, which are well correlated (Figure 6), are likely to include P bound to organic matter by Al (cf. Negrín et al. 1995), as well as phosphorus that binds organic matter to Al and Fe minerals (cf. Ognalaga et al. 1994). In any case, the adsorption of P in these soils appears to derive from a rapid formation of organic P complexes.

In young glacial till soils of Quebec, the concentration of leaf P in sugar maple (*Acer saccharum*) is negatively correlated to the levels of pyrophosphate-extractable Al and Fe in the upper layers of the soil (Paré & Bernier 1989), suggesting that P adsorption to humic materials limits P bioavailability. Rakata soils may be similar. Despite a high mean value of 100 μgP/g of plant-available P (Resin + HCO_3-extractable) in surface soils, the bioassay using upland rice suggests that P is deficient for plant growth on Rakata (Table 3). In contrast, on volcanic soils of Hawaii, a rapid release of P by rock weathering and the retention of P on organic materials leads to N limitations to plant growth at the earliest stages of soil development (Vitousek et al. 1993; Vitousek & Farrington 1997).

The estimated release of P by weathering of volcanic ash on Rakata, 0.05 to 0.22 g/m^2/yr (Figure 8), is greater than most values for P release by rock weathering reported in other forest ecosystems (Gardner 1990; Olsson & Melkerud 1989; Yanai 1992), perhaps reflecting rapid chemical weathering of fresh volcanic ash. Crews et al. (1995) also found that the loss of inorganic P (HCl-extractable) was associated with the accumulation of organic P in soils

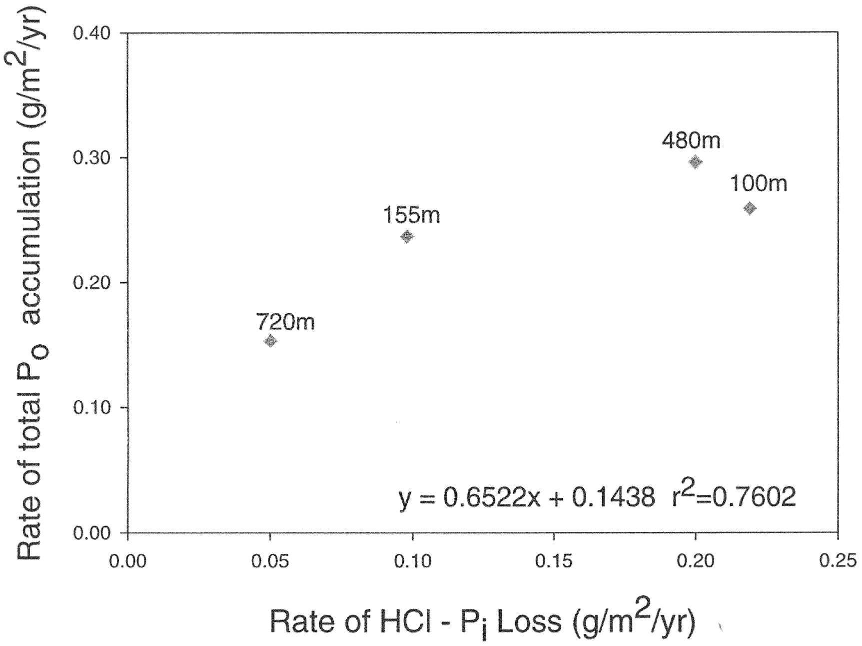

Figure 8. Correlation between the estimated rate of accumulation of organic P in the entire profile of 4 soils on Rakata and the estimated rate of loss of inorganic P extractable with HCl. The regression is not significant.

developing on lava flows on Hawaii. The estimated rate of accumulation of organic P in the soil profiles of Rakata is somewhat greater than the apparent release of P from rock weathering. Some of the discrepancy may result from errors in estimating total profile contents of P. However, a high rate of accumulation of organic P may cause P to be limiting to plant growth during early succession on the island, despite the high apparent rates of mineral weathering. Thus, our findings from Rakata do not support the generalization by Walker & Syers (1976) that N is limiting during the earliest stages of soil development, followed by P at later stages (Vitousek & Farrington 1997).

Acknowledgements

The field research could not have been completed without the helpful cooperation of L.I.P.I. (The Indonesian Institute of Sciences). We thank Dr. A.T. Kuiters (formerly of the Faculty of Biology, Vrije Universiteit, Amsterdam) for his advice on setting up the bioassay experiment and Professor W.H.O. Ernst for permission to use the greenhouse facilities. Olaf van der Kolk assisted with the data processing. We also thank Deborah Lawrence, Dan

Richter, Heather Viles, and Peter Vitousek for their critical reviews of an earlier draft manuscript. This is publication #51 of the Krakatau Research Programme of the University of Oxford. The full set of data for these and additional soil profiles on Sertung and Panjang are available from the senior author.

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