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9. ABSTRACT

This report gives examples of phosphate and sulfate sorption by soils from tropical areas; illustrates how sorption relates to the occurrence and composition of amorphous materials of soils; and shows how these curves can be used to evaluate fertilizer requirements and residual effects of fertilizers. The soil samples studied were surface soils from sugarcane fields on the island of Oahu, obtained along a transect of increasing rainfall. Results showed that phosphate sorption maxima were 300 µg P/g for a soil containing montmorillonite, and 1,320 µg P/g for a high-rainfall soil containing hydrated Al and Fe oxides. Amorphous materials removed from highly weathered soils were poor in Si as compared with the total soil. Gel-like coatings were seen in all soils examined. Treatments which removed these materials increased phosphate sorption but decreased sulfate sorption. Electron-micrographs suggested that P additions enhance formation of amorphous material. Phosphate sorption was closely related to silica-to-sesquioxide ratios of the extracted materials but not to amounts extracted. Sulfate sorption was very pH-dependent, while phosphate sorption was apparently much less influence by soil pH. Massive P applications to a soil rich in gibbsite continued to influence phosphate and sulfate sorption and crop growth 12 years after application.

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Phosphate and Sulphate Sorption by Latosols*

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ABSTRACT

Phosphate and sulfate sorption curves were constructed for soils collected along a transect of increasing rainfall. Phosphate sorption maxima were 300 μg P/g for a soil containing montmorillonite and 1320 μg P/g for a high rainfall soil containing hydrated Al and Fe oxides. Amorphous materials removed from highly weathered soils were poor in Si as compared with the total soil. Gel-like coatings were seen in all soils examined. Treatments which removed these materials increased phosphate sorption but decreased sulfate sorption. Electronmicrographs suggested that P additions enhance formation of amorphous material. Phosphate sorption was closely related to silica : sesquioxide ratios of the extracted materials but not to amounts extracted. Sulfate corption was very pH-dependent while phosphate sorption was apparently much less influenced by soil pH. Massive P applications to a soil rich in gibbsite continued to influence phosphate and sulfate sorption and crop growth 12 years after application.

Anion sorption reactions involving P and S are very important in highly weathered soils. The exchange complex of these soils has a large component of positive charge when the pH is low and opportunities for ligand exchange are enhanced by extensive surfaces low in Si. Phosphorus solubility in the highly weathered soils of Hawaii is very low. Phosphate sorption maxima for the more reactive soils are 10-20 times greater than those usually reported for soils of the Temperate Zone (Fox *et al.* 1968). The intensity of P retention by soils according to their mineralogy is : amorphous hydrated oxides> goethite-gibbsite>kaolin>2 : 1 clays. Since highly weathered soils tend to be P deficient, the question "Is P needed ?" scarcely needs be asked. A more appropriate question is "How much P do we need ?" Phosphate sorption isotherms are useful for this kind of evaluation.

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Sulfate sorption capacities can be very great for acid soils containing amorphous material. Sulfur deficiencies develop in these soils at levels of sorbed sulfate which are adequate for soils with low capacities to sorb sulfate.

Treatment of soils to remove amorphous materials rich in aluminum is reported to reduce the positive charge developed at low pH (Tweneboah *et al.* 1967). Recent electron microscope investigations have demonstrated widespread occurrence of amorphous, gel-like coatings of surfaces in Hawaii soils (Jones, 1970). In many soils these "gel-hulls" appear to envelop crystalline particles, which strongly suggests that they participate in surface reactions.

This report gives examples of phosphate and sulfate sorption by soils from tropical areas ; illustrates how sorption relates to the occurrence and composition of amophous materials of soils ; and shows how these curves can be used to evaluate fertilizer requirements and residual effects of fertilizers.

EXPERIMENTAL

Soil samples : Surface soil samples from sugarcane fields were secured along a transect of increasing rainfall on the island of Oahu. This set of samples has been used previously to study soil and plant Si (Fox *et al.* 1967).

Kapaa soil from Kauai was sampled in 1970 from plots fertilized with 0, 335, 670 and 1340 kg/ha P in 1958. No P has been applied since. Nine years of forage yield data from the test have been published. (Younge & Plucknett, 1966 ; Fox *et al.* 1968).

Sorption isotherms : Phosphate sorption isotherms were obtained by equilibrating 3-g samples of soil for 6 days at 25°C in 30 ml of 0.01 *M* $CaCl_2$ containing various amounts of $Ca(H_2PO_4)_2$ and two drops of toluene. Samples were shaken for 30 minutes twice daily. Phosphorus sorbed was plotted against P concentration in solution after equilibration. Sorption maxima were calculated using the linear form of the Langmuir isotherm (Olsen & Watanabe 1957). Data for sulfate sorption isotherms were obtained as for phosphate except that equilibration was for 24 hours with shaking for three 1-hour periods.

Removal of amorphous coatings : The procedure of Tweneboah *et al.* (1967) for extracting "active" aluminum from soils was used to remove amorphous materials. The method involves two 6-hour extractions with 0.5 *M* $CaCl_2$, pH 1.5 followed by several washings with 0.5 *M* $CaCl_2$ at pH 4.0 and pH 7.0. All extracts and washings were analyzed for Si, Al, Fe and Mn.

Electron microscopy : Selected soils were nebulized onto pure carbon substrates, and examined with a Hitachi HU-11A electron microscope. Surfaces relatively free of non-crystalline coatings produce particle images with virtually no gel-hull halo. There may be considerable electron beam damage, depending on the nature of surfaces. Particles thickly coated with gel-hulls may produce gel sputtering which is seen as dense rings at the outer margin of some gel-hull images. Since the appearance of electron-micrographs is related to sample conditions, all micrographs were obtained at the same magnification, beam intensity and beam exposure time.

RESULTS AND DISCUSSION

Examples of phosphate and sulfate sorption by soils of the tropics : Phosphate and sulfate sorption isotherms for selected soils (Fig. 1, A and B) illustrate the kind of variability covered by the term "Tropical soils". The soils of Figure 1A are phosphate deficient by any reasonable standard, yet the magnitude of the phosphate problem is vastly different for the several soils. For example, the soil from the sandy coastal plain of Queensland requires about 27 ppm P for legume establishment, which agrees well with P sorbed at 0.2 ppm P in the supernatant (Fig. 1A), which is 25 ppm. [The value, 0.2 ppm P in the supernatant, has been used to evaluate the P status of Hawaii soil (Fox *et al.* 1968)]. A 1200 ppm P requirement is indicated for the Hawaii soil, while actual P requirements for initial forage production were about 1100 kg/ha (Fox *et al.* 1968). These data indicate that the required level of P saturation (and thus P in solution) may be higher for soils which sorb small amounts of phosphate. Woodruff and Kamprath (1965) found that soils with low sorption capacities should be more highly P saturated than soils with high sorption capacities.

The soil from the Llanos of Colombia is typical of an extensive area of underdeveloped grassland in Colombia. The sorption curve predicts extreme phosphorus deficiency and a high phosphate requirement—these predictions have been confirmed by a few field trials in the area. Two lateritic soils of India are used for comparative purposes. They show that not all highly weathered soils have extremely high phosphate requirements.

Figure 1B gives sulfate sorption isotherms for selected soils. Pot studies in Hawaii indicate that S in the soil solution should be about 5 ppm for *Pennisetum clandestinum*—thus the reference line at 5 ppm S in the supernatant of Fig. 1B. Young corn growing on the Llanos soil from Colombia appeared to be sulfur deficient even though

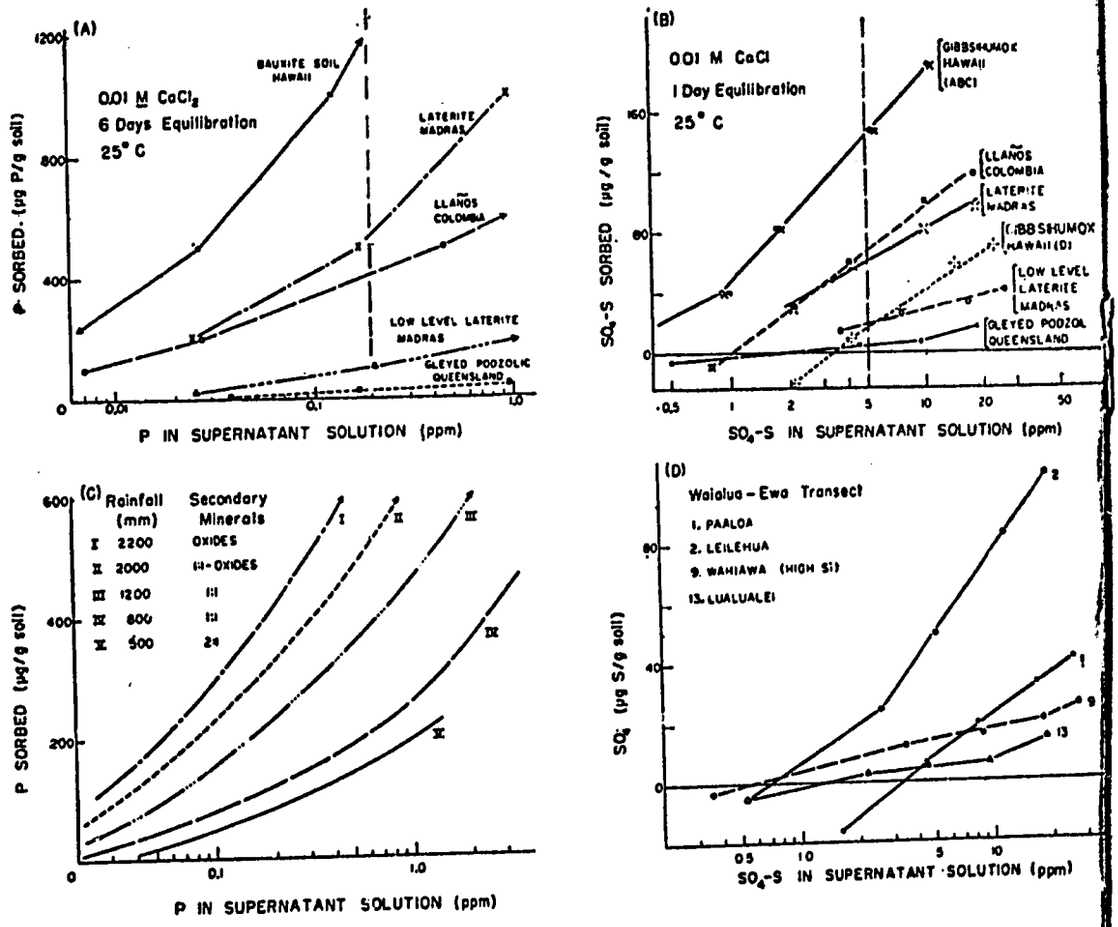
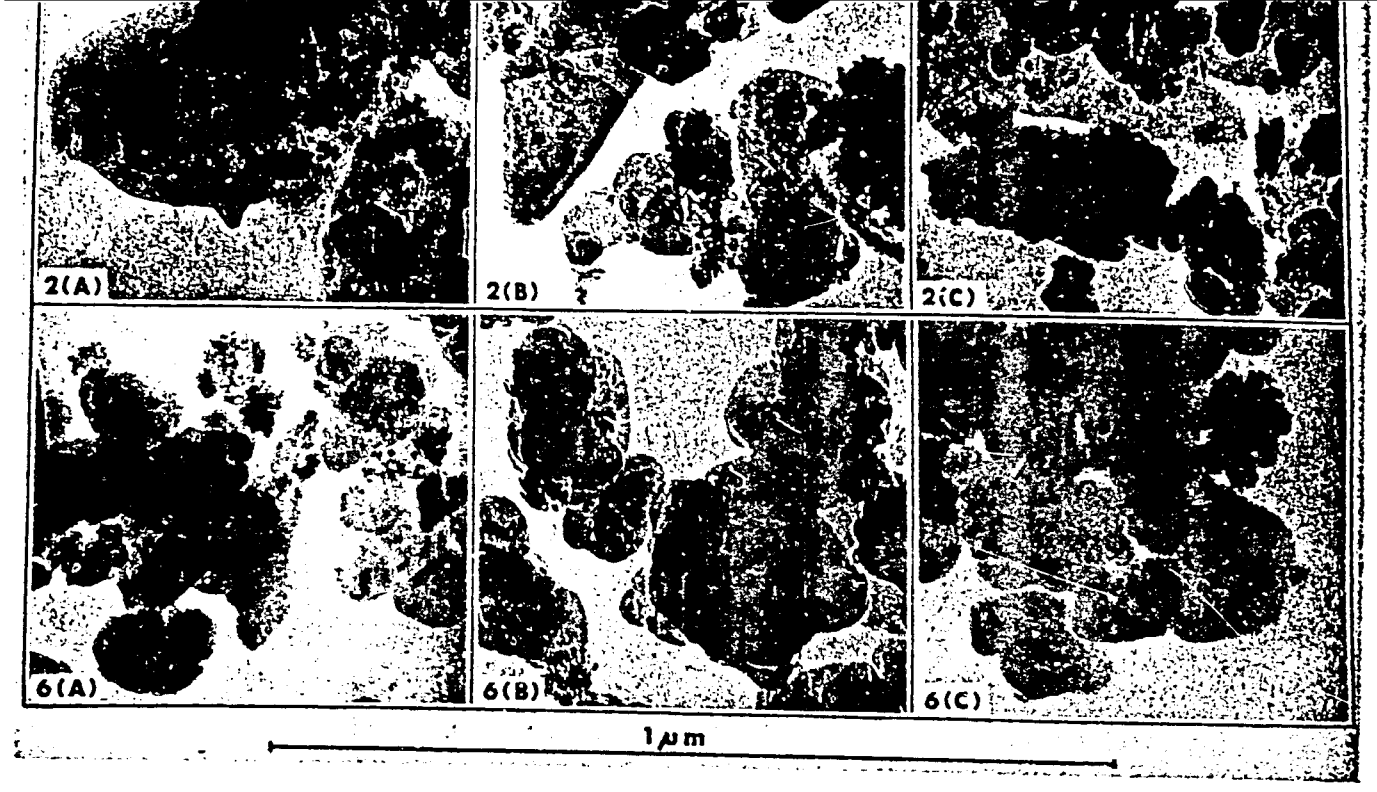


Fig. 1. Phosphate or sulfate sorption showing
(A) The diversity of phosphate sorption among soils of the Tropics.
(B) The magnitude of sulfate sorption by several highly weathered soils and the residual influence of P fertilizers on sulfate sorption by a Hawaii soil rich in gibbsite and amorphous oxides of Fe and Al.
(C) Phosphate sorption by soils sampled along a transect of increasing weathering. Each curve represents means for a group of similar soils along the transect.
(D) Sulfate sorption by selected soils along the transect. The Paaloa and Leilehua soils are similar except that the Paaloa soil (1) recently had been limed to pH 6.6.

sulfate had been applied. Figure 1B indicates probable deficiency since sulfate in solution at zero sulfur sorbed was 1 ppm and sorption at 5 ppm in solution was over 60 ppm. Sulfate sorption curves were remarkably similar in form to the phosphate sorption curves of


2(A)
2(B)
2(C)
6(A)
6(B)
6(C)
1 μm

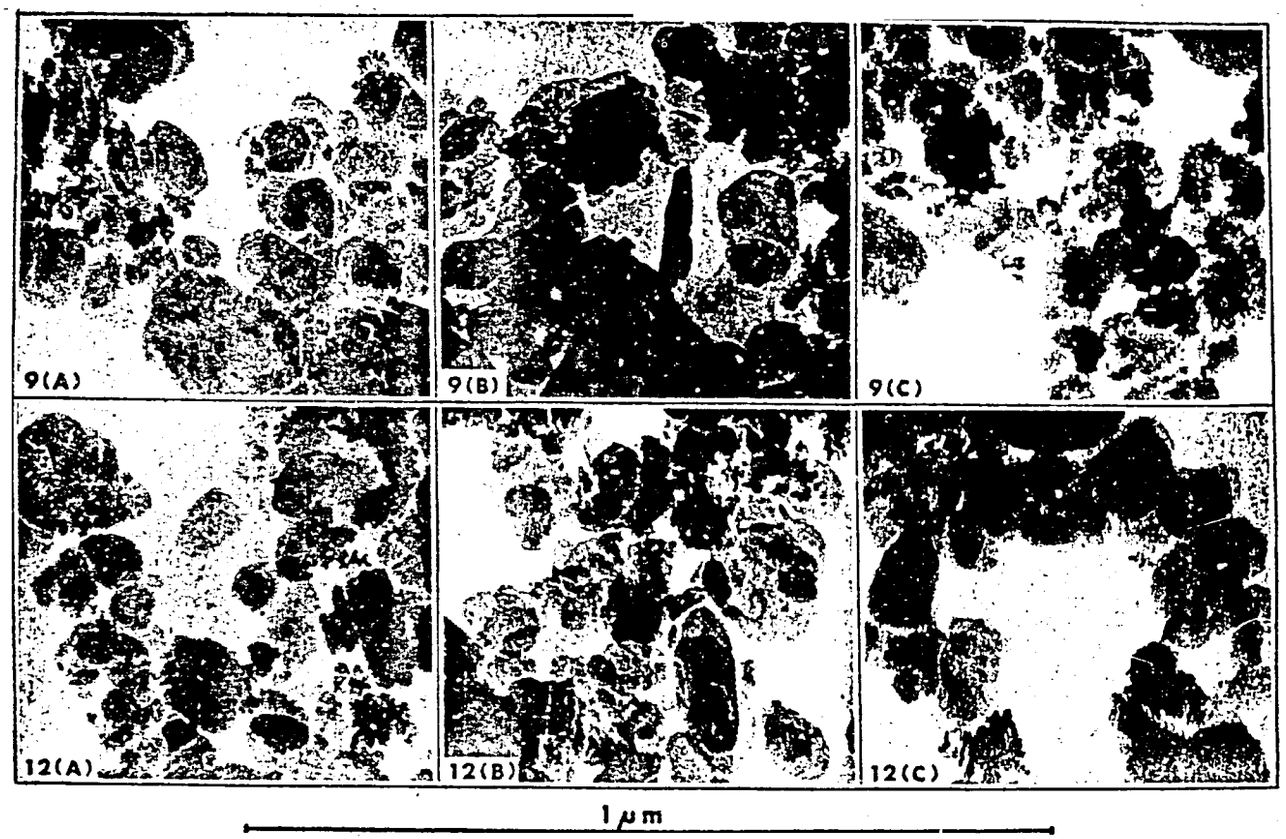


Fig. 2. Electronmicrographs of 4 soils.

(A) Before treatment to remove amorphous materials.

(B) After removal of amorphous material.

(C) After removal of amorphous material but with phosphate added at 800, 600, 500 and 600 μg P/g soil for soil 2, 6, 9 and 12, respectively. Soil numbers refer to site numbers in Table 1.

Fig. 1A, but sorption of P was greater than S sorption by an order of magnitude.

Phosphate and sulfate sorption along a transect of increasing rainfall: Climatic factors, especially rainfall, in Hawaii vary greatly over short distances, giving rise to great mineralogical diversity among soils of close proximity (Table 1). These soils sorb P in proportion to the extent to which they have been weathered (Fig. 1C). Sulfate sorption (Fig. 1D) was high only for highly weathered soils which were acid (site 2). Considerable amounts of sulfate could be desorbed from a highly weathered soil which had been limed (site 1).

Amorphous materials were evident in electronmicrographs of all soils examined (Fig. 2). These were abundant in the Leilehua soil from the high rainfall end of the transect (Fig. 2-2A), less obvious in the Molokai soil (Fig. 2-12A), and least obvious in two Wahiawa soils (Fig. 2-6A and 9A). After treatments to remove amorphous materials, electronmicrographs show relatively small amounts of gel present [See series (B) in Fig. 2, but especially the lower right quadrant of 9(B)]. All soils examined to date show an apparent increase in the amount of gel coatings after additions of phosphate as compared with samples treated to remove amorphous materials to which no P was added.

Table 1 presents data on the amount and composition of amorphous materials extracted with 0.5M $CaCl_2$ from soils along the transect. The amorphous materials from highly weathered soils were Si and P depleted. Relative to the silica : sesquioxide ratios of the total soil, the silica : sesquioxide ratios of extracted amorphous material were 0.1 to 0.2 for most highly weathered soils (Fig. 3A). Removal of amorphous coatings should increase the ratio and decrease phosphate sorption. Instead, P sorption was increased by this treatment which suggests that partial removal of agglutinating materials increased the amount of accessible particle surface.

Phosphate sorption was closely related to the silica : sesquioxide ratio of the amorphous coatings (Fig. 3B). The important factor in sorption was Si content of the coatings, rather than the amount of amorphous material (oxides removed, Table 1). Equilibration for longer than 6 days may give different results since diffusion of phosphate through gel materials probably is very slow.

Two Wahiawa soils (Table 1, sites 7 and 9) are very similar in most respects, but amorphous material in soil 9 contains almost twice as much Si as a result of having been irrigated with water containing 30 ppm Si as compared with water containing about 2.5 ppm Si for site 7. This difference, which was not eliminated by

TABLE 1

Total oxides removed and elemental composition of amorphous materials extracted by 0.5 M $CaCl_2$ from soils in relation to phosphate and sulfate sorption. Soils were sampled along a transect of increasing weathering, Oahu, Hawaii

Site No.	Rainfall (cm)	Soil[1] series and sub-group	Important[2] secondary minerals	pH	Composition of amorphous materials (ppm)					Oxides removed (%)	Phosphate adsorption		Sulfate sorbed at 5 ppm (μg/g)
					P	Si	Al	Fe	Mn		at 0.2 ppm (μg/g)	Max. (μg/g)	
13	50	Lu	M	7.6	270	3860	4300	1680	1170	2.11	85	300	4
12	60	Mo	K	7.8	110	1740	2310	770	1220	1.11	145	500	8
11	90	Kh	K, Gi	6.7	160	1720	2230	3050	1050	1.41	100	530	5
10	95	La	K	6.8	60	1180	2080	500	980	.86	145	525	19
9	100	Wa	K	6.8	160	1360	2610	340	1412	1.06	100	300	12
7	120	Wa	K	5.1	180	730	2630	550	1680	1.00	235	725	21
6	130	Wa	K	4.9	100	563	3000	560	1030	.93	280	770	29
5	170	Le	K	4.4	90	350	2560	1240	[illegible]	.82	330	910	13
4	220	Le	K, Gi	4.5	40	220	2100	970	410	.65	355	670	[illegible]
3	220	Le	K, Gi, I	5.0	20	230	2560	1740	410	.84	425	1020	34
2	230	Le	Gi, I	4.5	90	170	2200	3330	320	1.00	400	1000	49
1	230	Pa	Gi Go	6.6	20	200	1750	2090	410	.80	435	1320	8

[1] Lu=Lualualei (Typic Chromusterts), Mo=Molokai (Typic Torrox), Kh=Kawaihapai (Fluventic Oxic Eutropept), La=Lahaina (Typic Torrox), Wa=Wahiawa (Tropeptic Eutrorthox), Pa=Paaloa (Humoxic Tropohumult), Le=Leilehua (Humoxic Tropohumult).

[2] M = Montmorillonite, K = Kaolin, I = Illite, Gi = Gibbsite, Go = Goethite.

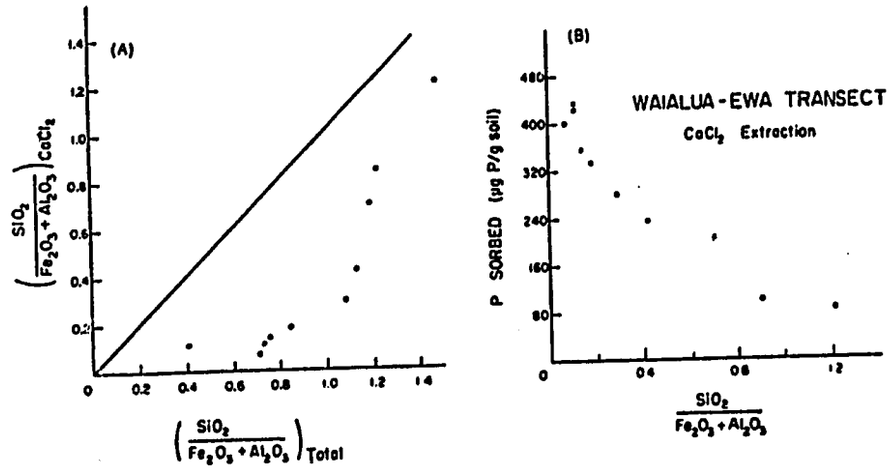


Fig. 3.
(A) The silica : sesquioxide ratio of amorphous materials extracted ($CaCl_2$ extracts) in relation to the ratio in the whole soil and
(B) Sorption of P in relation to the ratio in the amorphous material extracted.

$CaCl_2$ extraction, was associated with less phosphate sorption by soil 9 (Table 2).

Sulfate sorption was more closely related to soil pH ($r = -0.61^*$) than any other factor measured (Table 1, compare sites 1 and 2). Sorption decreased following removal of amorphous materials probably because of increased pH resulting from the final washings with neutral $CaCl_2$.

Residual effects of phosphate in highly weathered soils : In view of high phosphate sorption by highly weathered soils it is encouraging to observe that, after 12 years, massive phosphate applications to one such soil, a Gibbsihumox (Kapaa series), continues to influence phosphate sorption curves and maintain forage yields (Fig. 4). Although the rates of phosphorus applied were very great, Young and Plucknett (1966) have concluded that the costs can be amortized over several years. The Si status of the highly weathered Kapaa soil is exceedingly low and crops grown on this soil respond to silicate applications. Some, but not all, of this response can be attributed to improved P nutrition.

The data of Fig. 4A have some interesting implications about the influence of organic matter accumulation and/or soil desiccation on P sorption. The recently sampled (original) subsoil material sorbs much more phosphate than the non-phosphated sub-soil which has grown forage (although very little of it) for 12 years which, in turn, sorbs more P than the unfertilized top soil. It seems probable that

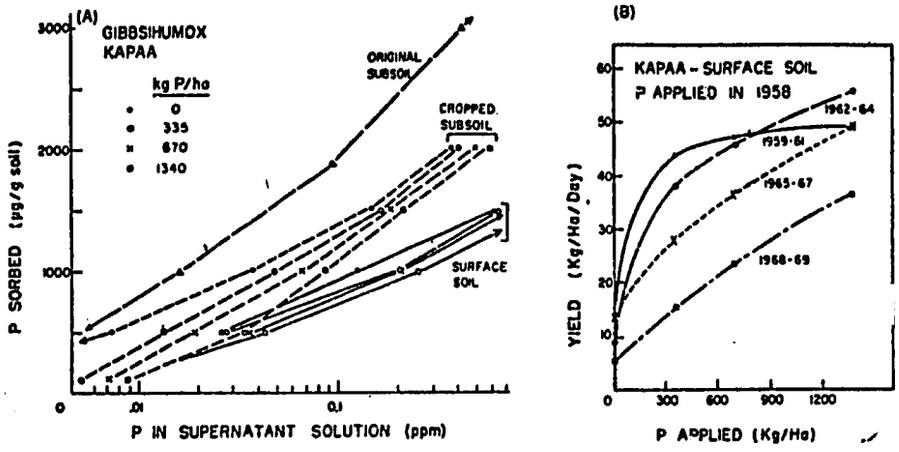


Fig. 4.

(A) Phosphate sorption by a surface soil and an exposed, cropped subsoil in relation to phosphate added 12 years earlier. The original subsoil shown for comparison had not been exposed, fertilized or cropped.

(B) Yields of dry forage (*Digitaria decumbens* plus *Desmodium* species) during 11 years in response to residual fertilizer P.

phosphate sorption sites are being blocked by organic anions. The effects of desiccation cannot be ruled out although rainfall at the experimental site is about 2500 mm.

Phosphate fertilizer applied at 1340 kg/ha 12 years ago depressed sulfate sorption by the Kapaa soil (Fig. 1B, Hawaii D) in comparison with the 0, 335 or 670 kg P/ha treatments (Fig. 1B, Hawaii A, B, C). This implies that most of the P had been precipitated or sorbed on sites which do not sorb sulfate. Repeated extraction of the original sub-soil material with phosphate gave 2900 ppm S. After 12 years the exposed low phosphate treated sub-soil contains about the original amount of sorbed sulfate. Only at the highest phosphate level does S seem to have been lost.

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