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9. ABSTRACT
Volcanic ash weathers quickly in the humid tropics and in a few years may develop an appreciable phosphorus adsorption capability. Apparently sulphate adsorption capacity develops more slowly. Phosphate and sulphate adsorption curves clearly reflect chemical and mineralogical changes in soils associated with weathering. For soils developed from ash (amorphous colloids) phosphate adsorption was related inversely to Si solubility. Phosphate adsorption by several oxisols of tropical America was 200 to 600 ug P/g soil at standard supernatant concentration (0.2 p.p.m.P). Capacity for P adsorption was 20, 425, 1900 and 2500 ug/g for the weathering sequence: fresh volcanic ash, Umbric Vitrandept, Typic Dystrandept and Oxic Dystrandept, respectively. Phosphate adsorption by andepts was related inversely to silicon solubility. Sulphate accumulates in large quantities in subsoils of the most highly weathered Oxisols and Dystrandepts. Some oxisols such as those of the Llanos Orientales of Colombia, generally are low in adsorbed sulphate throughout their profiles. Sulphur deficiencies in these soils can be expected if other limiting nutrition problems are corrected. The A horizon of Nipe soil was only three percent sulphate saturated and sulphate solubility was 0.4 p.p.m.. Mean SO_4-S saturation of subsurface horizons was 68 percent and mean solubility was 4.8 p.p.m.. Soils of the Llanos Orientales usually contained <10 ug/g of adsorbed S while mean adsorption capacity was about 150 ug/g. Volcanic ash soils retain sulphate in proportion to weathering but apparently sulphate adsorption capabilities develop more slowly than phosphate adsorption capability. Cation adsorption curves predict that suitable intensities of K and Ca nutrition can be reached with small additions of these cations to oxisols but that capacity for supply is low especially for soils of the Llanos Orientales. Attempts to stock these soils with cations may result in elevated soil solution concentrations, luxury uptake by plants and leaching. Aluminum dominates the exchange complex of soils

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of the Llanos Orientales.

*Examples of anion and cation adsorption by soils of tropical America**

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Volcanic ash weathers quickly in the humid tropics and in a few years may develop an appreciable phosphorus adsorption capability. Apparently sulphate adsorption capacity develops more slowly. Phosphate and sulphate adsorption curves clearly reflect chemical and mineralogical changes in soils associated with weathering. For soils developed from ash (amorphous colloids) phosphate adsorption was inversely related to Si solubility.

Phosphate adsorption by several oxisols of tropical America was 200 to 600 μg P/g soil at standard supernatant concentration (0·2 p.p.m. P). Capacity for P adsorption was 20, 425, 1900 and 2500 μg/g for the weathering sequence: fresh volcanic ash, Umbric Vitrandept, Typic Dystrandept and Oxic Dystrandept, respectively. Phosphate adsorption by andepts was inversely related to silicon solubility.

Sulphate accumulates in large quantities in subsoils of the most highly weathered Oxisols and Dystrandepts. Some oxisols, such as those of the Llaños Orientales of Colombia, are generally low in adsorbed sulphate throughout their profiles. Sulphur deficiencies in these soils can be expected if other limiting nutritional problems are corrected. The A horizon of Nipe soil was only three per cent sulphate saturated and sulphate solubility was 0·4 p.p.m. Mean SO_4-S saturation of subsurface horizons was 68 per cent and mean solubility was 4·8 p.p.m. Soils of the Llaños Orientales usually contained <10 μg/g of adsorbed S while mean adsorption capacity was about 150 μg/g. Volcanic ash soils retain sulphate in proportion to weathering but apparently sulphate adsorption capabilities develop more slowly than phosphate adsorption capability.

Cation adsorption curves predict that suitable intensities of K and Ca nutrition can be reached with small additions of these cations to oxisols but that capacity for supply is low especially for soils of the Llaños Orientales. Attempts to stock these soils with cations may result in elevated soil solution concentrations, luxury uptake by plants and leaching. Aluminium dominates the exchange complex of soils of the Llaños Orientales.

INTRODUCTION

Adsorption curves (isotherms) are useful for describing, studying and managing soils. First, they integrate and reflect many aspects of soil mineralogy, chemistry and past management of soils (FOX and KAMPRATH, 1970). Highly weathered volcanic ash retains phosphate very strongly and in great quantities (FASSBENDER, 1969; FOX, 1969). The same is true to a lesser extent for sulphate if

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the soil is acid (HASAN *et al.*, 1970; BORNEMISZA and LLANOS, 1966). Much less adsorption of these anions can be expected by kaolin clays and less still by expanding layer silicates. Cation adsorption generally follows a reverse pattern. Cation adsorption by highly weathered ash is so weak that cation leaching is a very real problem (FOX, 1969) although cation exchange capacity, as traditionally measured, may be very high in these soils.

Second, adsorption curves can be used to follow the course of soil development. Perhaps no better example can be given than phosphate adsorption by volcanic ash in the humid tropics where soil materials and climate promote rapid removal of silicon and accumulation of hydrated iron and aluminium oxides.

Third, adsorption curves provide background information about quantity-intensity relationships for adsorbed plant nutrients. This information is helpful for developing the three aspects of a complete soil testing programme: inventory, diagnosis and prescription.

Finally, adsorption curves yield data that can be used to calculate single-valued expressions such as BECKWITH's (1965) phosphate requirement or WOODRUFF's (1955) energy of exchange.

The purpose of this paper is to illustrate the points listed above, using data from soils of tropical America.

MATERIALS AND METHODS

Volcanic ash and ash derived soils

Mt Irazu (volcań Irazú) in Costa Rica erupted pyroclastic materials during the period 1963 to 1965. Ash material from this eruption was secured from Volio Farm during eruption in 1964 and again after eruption ceased in 1966. These samples were taken by Dr Elmer Bornemisza, IAIAS, Turrialba. Additional ash and ash derived soils of Costa Rica were sampled in 1969. Three of the soils sampled were described by KNOX and MALDONADO (1969) where they are listed as profiles 1, 2 and 4. The soils used for this study represent a weathering sequence as is indicated by the solubility of Si and degree of hydration of the soils. Colloids are mostly amorphous.

Soils from Colombia

The Eastern Plains (Llaños Orientales) of Colombia are a very large expanse of grassland bounded by the Andes mountains, Venezuela and the Amazon river basin. Soils are generally extremely infertile. Cattle grazing native vegetation present many nutritional problems. A series of samples were taken along an east west transect between the Meta and Guaviare rivers from La Libertad Experimental Station in the piedmont area east of the Andes to Las Gaviotes. Clays are predominantly the kaolin type but there are some 2:2 minerals (chlorite).

An example of soils of the intermountain valleys, tentatively classified as a Eutropept, was sampled from the Experimental Station Farm at Palmira in the Cauca Valley. The soil is a silty clay nearly saturated with Ca and Mg. Clays are the 2:1 swelling type.

Soils from Brazil and Puerto Rico

A Terra Roxa soil from Sao Paulo was included to represent kaolin clay iron

oxide systems. Nipe soil, a highly weathered oxisol, was obtained from Puerto Rico. This soil is not extensive in Puerto Rico but is important elsewhere in the Caribbean Islands, especially Cuba.

Adsorption isotherms

Data for plotting phosphate sorption curves were obtained by equilibrating 3 g samples of soil for six days at 25°C in 30 ml of 0·01 *M* $CaCl_2$ containing various amounts of $Ca(H_2PO_4)_2$. Equilibration was carried out in 50 ml plastic centrifuge tubes. Shaking was undertaken for periods of 30 min twice daily. Toluene was added to suppress microbial activity.

Sulphate sorption procedures were the same as for phosphate except that Na_2SO_4 replaced the phosphate and equilibration was for one day with continuous shaking.

Potassium and calcium adsorption was in 0·0025 *N* Cl solutions of K and Ca. Equilibration time was one day and the soil solution ratio was 1:10.

Soil extraction procedures

Silicon was determined in saturation extracts of soils. Soil samples (50 cm^3 volume) were placed in leaching tubes with free drainage. Water was added in small increments until the first leachate appeared. The columns were allowed to equilibrate for three days after which small aliquots of water were added. The first 8 ml of leachate were centrifuged and appropriate aliquots were used for colorimetric determination of Si.

Sulphate was extracted by repeated batch treatments of soils with 500 p.p.m. P as $Ca(H_2PO_4)_2$ in a soil solution ratio of 1:5. Previous work (HASAN *et al.*, 1970) had demonstrated that four extractions desorb most of the sulphate from subsoil materials.

Exchangeable cations were extracted with neutral 1 *N* NH_4OAc except that Al was extracted with 1 *N* KCl.

RESULTS AND DISCUSSION

Phosphate adsorption

The importance of soil mineralogy in controlling soil chemistry is illustrated by the marked differences in phosphate adsorption characteristics of the different volcanic ash materials represented here. Volcanic ash weathers rapidly to form amorphous materials which adsorb phosphate in proportion to the extent of silicon depletion. When the ash is finely divided, as was the case with ash carried by water to the floor of Irazú Crater, an appreciable phosphate capacity developed in only four years (*Figure 1*). Even coarse material of the crater rim adsorbed 75 p.p.m. P at standard P concentration (0·2 p.p.m. P in solution). Ash of the same age deposited over a soil (Umbric Vitrandept) about 2 km from the crater adsorbed less phosphate than materials from the crater rim. The most obvious explanation is the effect of organic residue which had already developed in the young ash. There was no vegetation in the crater.

The outstanding difference in phosphate adsorption among soils as presented in *Figure 1* is associated with weathering which is a function of climatic factors and time. Phosphate adsorption at standard concentration was 20, 425, 1900 and 2500 μg/g for the new ash, Umbric Vitrandept, Typic Dystrandept and Oxic

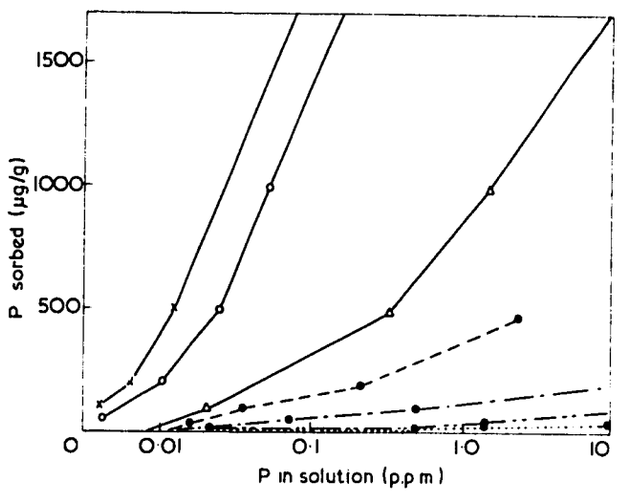

Figure 1. Phosphate sorption by volcanic ash and ash derived soils of Costa Rica showing how the soils and ash fall into a weathering sequence. ·, Typic Dystrandept; x, Oxic Dystrandept; ·, Umbric Vitrandept, · · , fine ash from crater, · · ·, cinder from rim, · · · · , ash over soil, ... fresh ash

Dystrandept respectively. Weathering produced a marked decrease in the solubility of Si in these soils (*Table 1*).

The ease with which Si is weathered from volcanic ash, as indicated here, emphasizes the rejuvenating effects which can be expected when fresh ash is deposited on more highly weathered soil. In Hawaii the Si content of irrigation water can increase the soluble Si of soils and thereby decrease phosphate adsorption (FOX *et al.*, 1971). Similar effects should result from the weathering and leaching of an ash mantle.

Phosphate adsorption by representative soils from the Llaños Orientales, the Cauca Valley, Brazil and Puerto Rico is compared in *Figure 2*. The Typic Dystrandept from Costa Rica is also included to give a wide range in mineralogical systems. Phosphate adsorbed at standard concentration is presented in relation to Si in saturation extracts in *Table 2*. Soils which are predominantly expanding silicate clays and have high Si solubility adsorb little

Table 1. Phosphate adsorption at supernatant concentration of 0·2 p.p.m. P by volcanic ash and ash derived soils which have been variously depleted of Si by weathering

Soil	*Phosphate adsorbed (µg P/g)*	*Si saturation extract (p.p.m.)*	*Field soil moisture (%)*	*Rainfall (mm)*	*Temp. (°C)*
Cinder (crater rim)	20	46·2			
Ash, 4–6 year	20	12·5	15	2000	9
Umbric Vitrandept	425	18·8	14	2000	9
Typic Dystrandept	1900	5·7	77	2000	19
Oxic Dystrandept	2500	1·5	116	3800	21

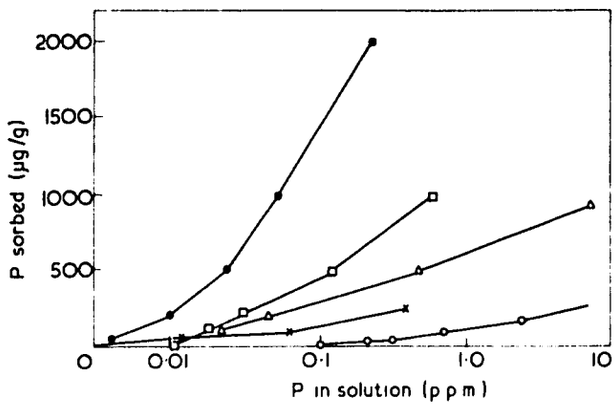

Figure 2. Phosphate sorption by a diverse group of soils from tropical America. Phosphate sorbed for the mineralogical systems represented is in the following sequence: amorphous oxides > crystalline oxides > kaolin clays > 2:1 clays. ●, Typic Dystrandept; □, Nipe; △, Llanos; ×, Terra Roxa; ○, Cauca Valley

phosphate at standard concentrations. With increasing weathering, as indicated by decreasing Si solubility, phosphate adsorption increases. Andept soils are in a class apart as far as phosphate adsorption is concerned.

In Hawaii, phosphate adsorption values can be converted into phosphate fertilizer requirements with a fair degree of precision if corrections are made for bulk density of soils and allowance is made for plant species effects. Maize and sorghum require about 0·06 p.p.m. P in solution for 95 per cent of maximum yield whereas phosphate-sensitive crops such as leafy vegetables usually require 0·1 to 0·4 p.p.m. A number of perennial crops apparently have a very low P requirement after the initial establishment stage is past. Present indications are that sugar-cane, bananas, and tropical forages, such as Pangola grass and *Desmodium* spp., have requirements which are lower than maize.

Table 2. Phosphate adsorption at supernatant concentration of 0·2 p.p.m. P and phosphate and silicon solubility of selected soils from tropical America

Location	*Soil classification*	*Phosphate adsorbed (µg P/g)*	*Si in saturation extract (p.p.m.)*	*Soluble P in 0·01 M $CaCl_2$ (p.p.m.)*
Cauca Valley	Eutropept	25	19·4	0·10
Brazil (Terra Roxa)	Oxisol	200	8·9	0·03
Llanos Orientales				
La Libertad	Oxisol	400	7·0	<0·01
La Concordia	Oxisol	300	6·8	<0·01
Carimagua	Oxisol	380	13·7	<0·01
Puerto Rico (Nipe)	Oxisol	600	1·3	0·01
Costa Rica	Typic Dystrandept	1900	5·7	<0·004
	Oxic Dystrandept	2500	1·5	<0·004

Table 3. Extractable SO_4-S in profiles of volcanic ash derived soils of Costa Rica

1963–65 Ash		*Umbric Vitrandept**		*Typic Dystrandept*		*Oxic Dystrandept*	
Depth (cm)	*SO_4-S (p.p.m.)*	*Depth (cm)*	*SO_4-S (p.p.m.)*	*Depth (cm)*	*SO_4-S (p.p.m.)*	*Depth (cm)*	*SO_4-S (p.p.m.)*
0–13	10	13–35	18	0–30	48	0–38	112
		35–50	0	45–75	20	38–60	258
		50–90	0	80–90	92	90–110	412
		105–120	18	160–180	42	165–180	508

*The Umbric Vitrandept was covered by 13 cm of 1963–65 ash

Sulphate adsorption

Sulphate adsorption is an important feature of highly weathered soils. It is responsible for sulphate accumulation to very high levels in some soils, especially weathered Andepts and other soils which contain gel-like materials. This is illustrated in *Table 3*. Sulphate does not accumulate in large amounts in profiles developed in volcanic ash until weathering is well advanced.

Sulphate distribution in the Nipe profile is typical of the highly weathered Oxisols examined. Distribution of sulphate in the profile, solubility of the native sulphate, as determined from the isotherms at no change in SO_4 adsorption, and sulphate required to adjust the equilibrated soil solution to 5 p.p.m. S are given in *Table 4*. Sulphate adsorption maxima, the reciprocal slope of the linear form of the Langmuir adsorption curve, increased with depth in the profile. Adsorbed sulphate (phosphate extractable S) also increased with depth but saturation percentage was maximum in the 45 to 70 cm depth increment. If the soil material is constant, sulphate solubility is a function of the degree of sulphate saturation of colloids. The fact that sulphate solubility continued to increase after the saturation percentage began to decrease is evidence that saturation percentage may not be an adequate expression of sulphate availability. For Andepts in Hawaii sulphate sulphur solubility was about 5 p.p.m. when saturation was 60 to 80 per cent (HASAN *et al.*, 1970). Sulphur nutrition is probably on the borderline of deficiency for some crops when soil solutions contain 3 to 5 p.p.m. SO_4-S.

Table 4. Distribution, solubility and adsorption or desorption of sulphate sulphur in relation to sulphate adsorption maxima in a Nipe soil profile

Depth increment (cm)	*Phosphate extractable sulphate (p.p.m.)*	*Sulphate solubility (p.p.m.)*	*Sulphate requirement* (p.p.m.)*	*SO_4-S adsorption max (p.p.m.)*	*SO_4-S saturation (%)*
0–25	40	0·4	94	200	20
25–40	255	1·8	44	362	70
45–70	373	1·1	35	433	86
70–95	463	4·6	20	765	61
90–120	792	8·6	100	1250	63
120–160	1234	7·8	150	2136	58

*Sulphate sulphur adsorbed by the soil equilibrated with 5 p.p.m. SO_4-S in the supernatant solution. Negative values refer to predicted SO_4-S release if SO_4 is desorbed to 5 p.p.m. in solution.

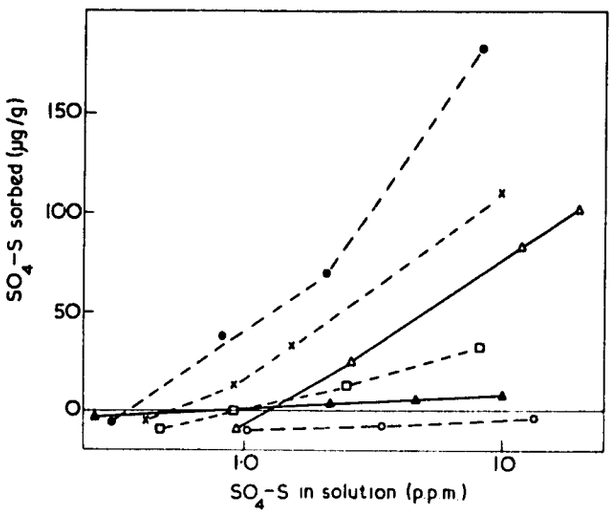

Figure 3. Sulphate sorption by a group of diverse soils from tropical America. Sulphate adsorption for the mineralogical systems represented is in the following sequence amorphous hydrated oxides > crystalline oxides > kaolin clays > 2:1 clays. ●, Typic Dystrandept; x, Nipe; ○, Llanos Carimagua; □, Terra Roxa; ▲, Eutropept; △, 1963 65 ash

Sulphate is readily desorbed from soils by phosphate and by hydroxide. It is probable that organic anions also compete for adsorption sites with sulphate and this may account for the low sulphate status of most surface soils.

Upland soils of the Llanos of Colombia contain very little adsorbed sulphate, the mean SO_4-S adsorption maximum is about 150 µg/g and sulphate solubility is low (data not shown). These soils require about 60 µg S per gramme of soil to attain 5 p.p.m. S in solution (*Figure 3*). At present low levels of production, there is probably sufficient S in rain and from mineralization of organic matter to meet plant needs. By any higher standard these soils should be sulphur deficient.

Potassium calcium adsorption

Recent evidence supports the concept that nutrient uptake by plants is mostly controlled by the composition of soil solutions. Thus GRIMME *et al.* (1971) reported that oats growing in 20 different potted soils (illitic, chlorotic and kaolinitic) required from 0·5 to 0·8 mequiv./l K in the soil saturation extract for maximum yield. A recalculation of Hawaii data (GRAHAM and FOX, 1971) indicates maximum yield at about 0·8 mequiv./l K for 11 soils of Hawaii (amorphous gels, oxides, 2:1 layer silicates and kaolinitic). The agreement is remarkable considering the diversity of soils used. Field evidence suggests lower requirements for K in solution. WOODRUFF and McINTOSH (1960) reported that maize did not respond to applied potash when K in 0·01 *M* $CaCl_2$ was 9 p.p.m. (0·23 mequiv./l). BARBER *et al.* (1963) measured the composition of saturation extracts of soils growing maize. Median K content was 0·1 mequiv./l. In Hawaii there is evidence that borderline K deficiency for banana is associated

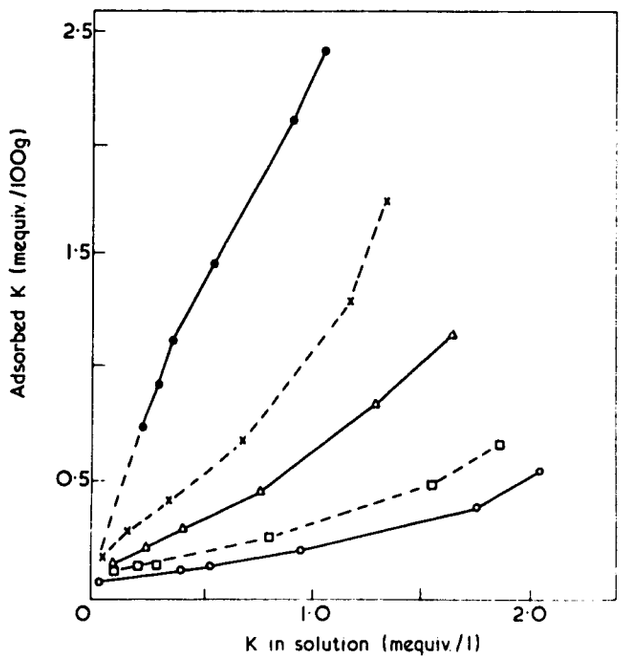

Figure 4. Potassium on the exchange complex of selected soils of tropical America in relation to equilibrium concentrations of K in solution. Adsorbed K represents the algebraic sum of exchangeable K originally present and K adsorbed or desorbed during equilibration with solutions which were 0·0025 N Cl as K and/or Ca. •, Eutropept Cauca Valley. x, Oxic Dystrandept. ▫, Terra Roxa. ○, Nipe. △, Llanos Carimagua

with an equilibrium concentration of about 0·2 mequiv./l K in 0·01 *M* chloride. For 0·0025 *N* chloride solution, equilibrium K was 0·1 mequiv./l for the borderline deficient situation.

POPENOE (1960) has pointed out that calculations of percentage base saturation of the exchange complex give no measure of the absolute quantities of nutrient available for plant growth. Base saturation information must be interpreted in terms of clay mineral types. The same is not true if cation data are presented as adsorption curves either with initial exchange cations added as in *Figure 4* or without as in *Figure 5*. Such curves are useful for seeing quantity- intensity relationships more clearly. If 0·1 mequiv./l K (in 0·0025 *M* Cl) is taken as borderline K deficient, the following required levels for exchangeable K are obtained for the soils in *Figure 4*:

Soil	*K (mequiv./100 g)*
Llaños (Carimagua)	0·10
Nipe	0·12
Terra Roxa	0·15
Oxic Dystrandept	0·24
Cauca Valley	0·40

The intensity of K nutrition, the buffering capacity of soils, and fertilizer requirements for attaining specified levels of K in solution are more easily seen in *Figure 5*. Apparently the Nipe soil is potassium deficient, the Dystrandepts are borderline, the soils from Colombia are adequately supplied and the Vitrandept will supply potassium in excess. The instantaneous K level (intensity) can be distinguished from supplying power (quantity). *Figure 5* predicts that the Eutropept of the Cauca Valley will not be deficient until 0·4 mequiv. K/100 g soil has been depleted while for the Llanos (Carimagua) soil deficiency can be expected after 0·04 mequiv. K has been extracted.

Exchangeable calcium was very low in the highly weathered soils (*Table 5*), and Ca in 0·0025 *M* KCl solutions equilibrated with these soils was as low as 0·005 mequiv./l for the Oxic Dystrandept and 0.02 mequiv./l for a soil from the Llanos Orientales. Aluminium was the most abundant exchange cation in soils of the Llanos Orientales and in one soil (La Concordia) its concentration in equilibrated solutions exceeded calcium ninefold.

Energies of replacement of K by Ca + Mg were calculated as suggested by WOODRUFF (1955) except that values for Ca and K in solutions were secured from adsorption curves at zero change in cation adsorbed and Mg was that in equilibrium with 0·0025 *M* KCl. These values are presented in *Table 5*. WOODRUFF and McINTOSH (1960) suggested that 3500 cal/mol would provide adequately for the K nutrition of plants. Very low values may represent either K excess or Ca + Mg deficiency. The latter interpretation probably fits best for the highly weathered soils investigated in this study since Ca in equilibrated 0·0025 *M* Cl solutions was as low as 0·005 mequiv./l (data not shown), while K in excess is likely in the Vitrandept.

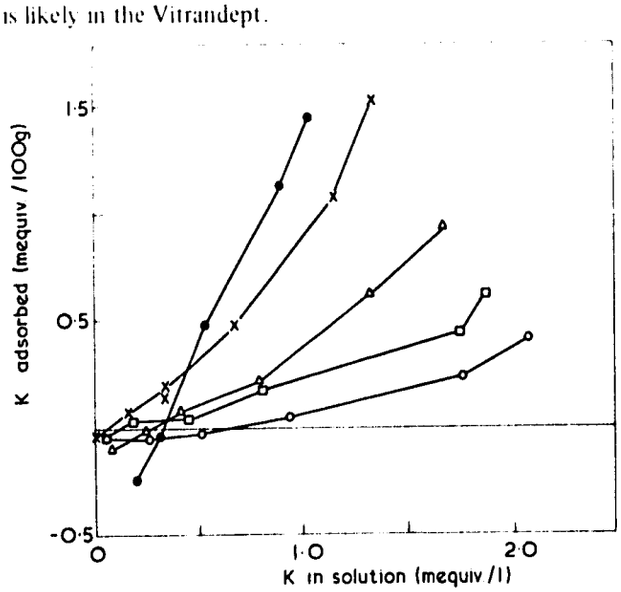

Figure 5. Potassium sorbed by selected soils of tropical America in relation to concentrations of K in solution following equilibrations with solutions which were 0·0025 N *Cl as K and/or Ca.* ●, *Eutropept Cauca Valley* x, *Oxic Dystrandept;* △, *Terra Roxa;* □, *Nipe;* ○, *Llanos Carimagua*

REFERENCES

BARBER, S.A., WALKER, J.M. and VASEY, E.H. (1963). 'Mechanisms for the movement of plant nutrients from the soil and fertilizer to the plant root.' *J. Agric. Food Chem.* **11**, 204–206

BECKWITH, R.S. (1965). 'Sorbed phosphate at standard supernatant concentration as an estimate of the phosphate needs of soils.' *Aust. J. Exp. Agric. Anim. Husb.* **5**, 52–58

BORNEMISZA, E. and LLANOS, R. (1966). 'Sulfate movement, adsorption and desorption in three Costa Rica soils.' *Proc. Soil Sci. Soc. Am.* **31**, 356–360

FASSBENDER, H.W. (1969). 'Phosphorus deficiency and fixation in volcanic ash soils in Central America.' *Panel on Volcanic Ash Soils in Latin America, Turrialba, Costa Rica* **B4**, 1–10

FOX, R.L. (1969). 'Fertilization of volcanic ash soils in Hawaii.' *Panel on Volcanic Ash Soils in Latin America, Turrialba, Costa Rica* **C6**, 1–13

FOX, R. L., HASAN, S. M. and JONES, R. C. (1971). 'Phosphate and sulfate sorption by latosols.' *Proc. Int. Symp. Soil Fertility Evaluation, New Delhi* **1**, 857–864

FOX, R.L. and KAMPRATH, E.J. (1970). 'Phosphate sorption isotherms for evaluating the phosphate requirements of soils.' *Proc. Soil Sci. Soc. Am.* **34**, 902–907

GRAHAM, E.E. and FOX, R.L. (1971). 'Tropical soil potassium as related to labile pool and calcium exchange equilibria.' *Soil Sci.* **111**, 318–322

GRIMME, H., NEMETH, K. and BRAUNSCHWEIG, L.C.V. (1971). 'Some factors controlling potassium availability in soils.' *Proc. Int. Symp. Soil Fertility Evaluation, New Delhi* **1**, 33–43

HASAN, S.M., FOX, R. L. and BOYD, C.C. (1970). 'Solubility and availability of sorbed sulfate in Hawaiian soils.' *Proc. Soil Sci. Soc. Am.* **34**, 897–901

KNOX, E.G. and MALDONADO, P. (1969). 'Soils from volcanic ash. Excursion from Turrialba to Volcan Irazú.' *Panel on Volcanic Ash Soils in Latin America, Turrialba, Costa Rica* **A8**, 1–7

POPENOE, H. (1960). 'Some soil cation relationships in an area of shifting cultivation in the humid tropics.' *Trans. 7th Int. Congr. Soil Sci., Madison* **2**, 303–311

WOODRUFF, C.M. (1955). 'The energies of replacement of calcium by potassium in soils.' *Proc. Soil Sci. Soc. Am.* **19**, 167–171

WOODRUFF, C.M. and McINTOSH, J.L. (1960). 'Testing soil for potassium.' *Trans. 7th Int. Congr. Soil Sci., Madison* **4**, 80–84

DISCUSSION

A.V. Downer: Would you care to comment on the significance of pH in relation to the sorption mechanisms you have described?

Author's reply: We have examined phosphate adsorption at three pH levels using a Gibbsihumox. We took care to keep Ca added constant by balancing $Ca(OH)_2$ with $CaCl_2$. Under these conditions one isotherm described all of the data points. The pH range was about 5·0 to 6·5.

H. Vine: In carrying out these equilibration studies, especially with Andosols, can one use dried soil prepared and kept in the normal manner?

Author's reply: As a general practice we keep these soils in a moist condition. The Hydrandepts dry irreversibly so we have assumed that phosphate sorption would decrease upon drying. This may not be true. We once dried a Hydrandept to varying degrees over a short period of time and did not find loss in sorption capacity. The results may have been different if drying had been done slowly or if there was alternate wetting and drying.

Lj. Nalovic: On which criterion did you base your conclusion that the adsorption of P and SO_4 or Si take place with 'gel hulls' rather than chemical reaction.

Author's reply: I am not trying to distinguish between the various mechanisms by which phosphate or sulphate may be retained by soil. This is the reason I define sorption as 'that which has disappeared from solution'.

Lj. Nalovic: Did you measure the specific surface of samples before and after the treatment. I agree with you that the hydrated surface of iron and maybe aluminium oxides adsorb cations and anions from solution where they

are more easily desorbed than in the case of chemical reactions such as Fe-O-P etc.

Author's reply:– We did not measure specific surfaces. We have looked at the thickness of 'gel-hulls' in relation to phosphate applications and believe there is some increase in thickness as a result of applying P. This does not necessarily mean that specific surface will be increased. It may in fact decrease if the gel material has an agglutinating effect.

G.T. Felbeck: If an oxisol is pretreated with a soluble silica source does this reduce the phosphate adsorption by these soils?

Author's reply:– We have evidence that this is the case at least in some instances. Calcium silicates are used by the sugar-cane industry in Hawaii. We think that improved phosphorus nutrition is one of the factors responsible for improve ! yields obtained as a result. There also seems to be other factors involved, however.

B.H. Janssen: Do you think the determinations of P adsorption isotherms can be used on a practical scale for fertilizer recommendations?

Author's reply: So far we have not used adsorption curves in a routine way. I think they could be done although more work will need to be expended than for most of the methods now used. The isotherm need not have so many points on it. In fact only one point may be sufficient if a 'standard curve' for the specific soil is available to establish the slope.

B.H. Janssen: There is a method identical or nearly identical with your method where some standard value such as a ratio at a fixed concentration of the solution is used for advisory work. What is your comment?

Author's reply: I am not familiar with the work to which you refer. The problem of different adsorption values for different equilibration ratios has been investigated but the explanations given are not very satisfying. I think that an increase in adsorption with increasing soil solution ratio should be expected because increasing the ratio will increase desorption of sulphate, silicate and perhaps organic anions. This should be accompanied by equivalent phosphate adsorption increase.