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MINERALOGY AND BEHAVIOR OF TROPICAL SOILS

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This paper describes the behavior of a group of mineralogically unique soils, tropical soils for which there exists a minimum of transferable data. While they are not typical of all tropical soils, the large majority of soils in and out of the tropics possesses similar features. A fundamental property of a soil mineral is the sign and magnitude of the charge on its surface. In many layered silicates, the sign and magnitude of the electrical charge is constant. In other minerals, surface charge arises from adsorption of potential-determining ions or specific absorption of impurities. Minerals which are commonly found in tropical soils and which behave as variable charge colloids are the crystalline and non-crystalline oxides and hydrous oxides of silicon, aluminum, iron, manganese and titanium. Non-crystalline alumino-silicates also behave as variable charge colloids. In soils with variable charge minerals, specific absorption of anions causes the cation exchange capacity to decrease. For these soils, prediction of soil behavior will be improved if a model based on variable charge colloid is used.

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MINERALOGY AND BEHAVIOR OF TROPICAL SOILS

G. Uehara, L. D. Swindale, and R. C. Jones

INTRODUCTION

Extrapolation of temperate climate experience to the tropics has met with varying success. There is general concensus among agricultural scientists who work in the tropics that the quantity of transferable information lies somewhere between wholesale acceptance and total rejection. The demarcation between these extremes is not invariant; it varies from soil to soil.

Soil mineralogy is one of several parameters which can be used to define more precisely the kinds of data which can be transferred from one region to another. The transfer of information should be from temperate to tropical as well as in the reverse direction. Of equal and more immediate value is the transfer process within the tropics. In cases where no transferable information is available, generation of new information is absolutely essential.

The purpose of this paper is to describe the behavior of a group of mineralogically unique soils. These are tropical soils for which there exists a minimum of transferable data. While they are not typical of all tropical soils, the large majority of soils in and out of the tropics possesses similar features to some degree.

MINERALOGY OF TROPICAL SOILS

Tropical soils contain most or all of the common minerals identified in temperate region soils, and in addition, many which occur rarely in the latter.

The chart in Table I lists most of the common minerals which are found in soils throughout the world. Minerals which are frequently found in quantity in tropical soils, but which rarely occur in abundance in temperate regions are the oxides and hydrous oxides of iron, aluminum, manganese and titanium. It is possible to extrapolate temperate climate experience to the tropics when a tropical soil consists mainly of phyllosilicates. Temperate climate experience fails when applied to soils which are predominantly oxide and hydrous oxides of iron and aluminum in mineralogy. For these soils, there is little temperate climate experience to transfer.

CHEMISTRY OF OXIDE MINERALS

Most soils contain mixtures of colloids of the constant charge and variable charge types. Implicit in nearly all soil research is the assumption that soil colloids behave and respond as constant charge materials. For most soils in temperate regions, this is a valid assumption. In the layered silicates, attapulgite and zeolites, surface charge arises from isomorphous substitution of ions in the lattice interior, and the charge is relatively independent of the conditions in the soil solution.

In oxide systems the electrical charge arises from adsorption of ions on particle surfaces. These ions are called potential-determining ions and include the hydrogen and hydroxyl ions as well as the metal ions which

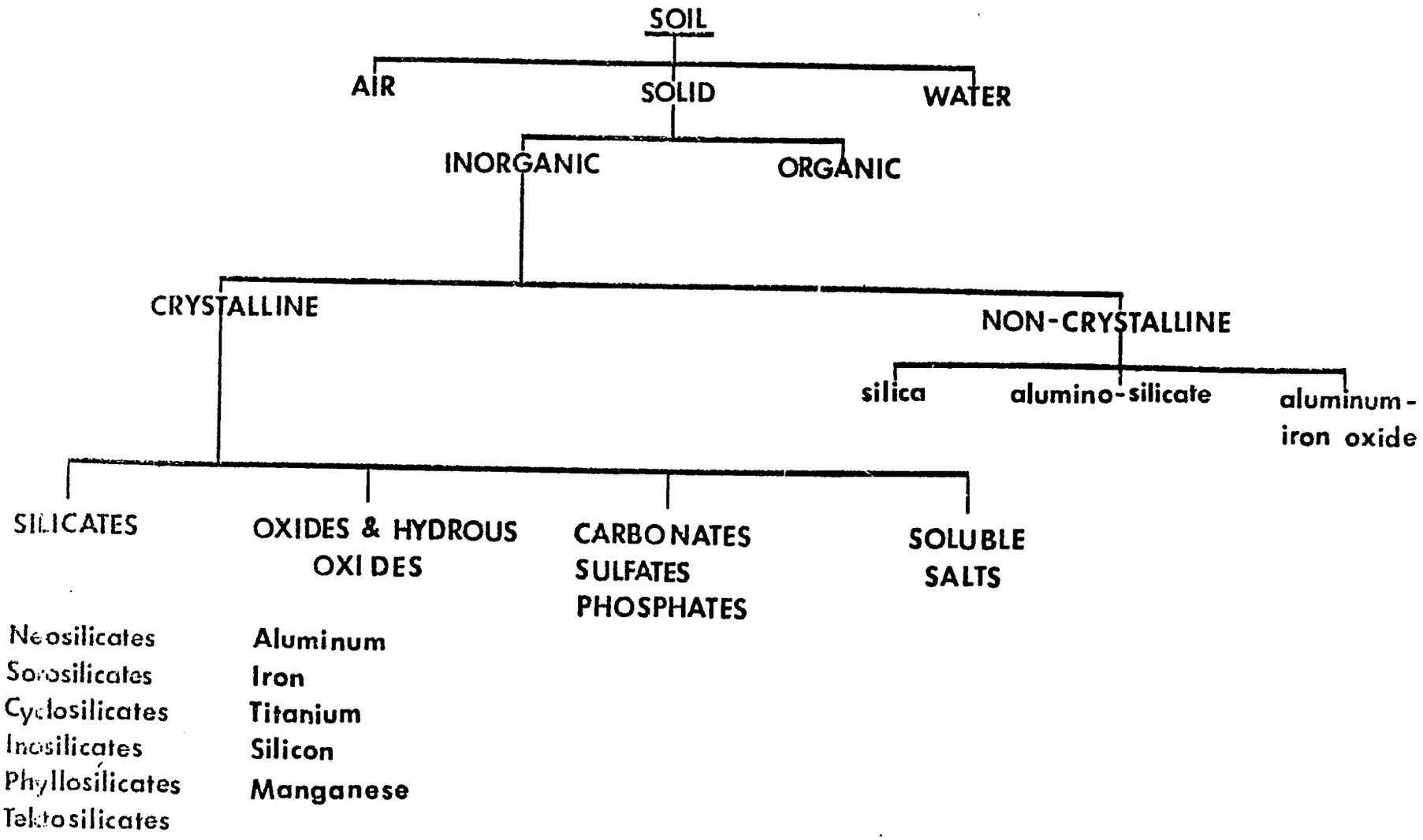

Table 1. Soil Composition. Tropical soils generally have higher oxide and hydrous oxide content than soils of the temperate regions. Non-crystalline materials are also abundant in some tropical soils.

make up the lattice (Parks and de Bruyn, 1962). An important consequence of this is that in oxide systems of iron and aluminum, for example, the ions of iron or aluminum are not exchangeable but potential-determining ions.

While colloids of constant charge and variable charge types differ in overall behavior, a single expression can be used to describe both systems. The relationship between surface charge σ and surface potential Φ_o is

$$\sigma = \frac{kD}{4} \Phi_o \tag{1}$$

where D is the dielectric constant of water and k is the reciprocal of the double layer thickness. This limiting equation applies when the surface potential is less than 25 millivolts. A more rigorous and non-linear form of equation 1 should be used for higher potentials, but equation 1 is more useful for purposes of discussion.

In colloids with constant charge surfaces, a change in the electrolyte concentration of the soil solution causes k to change, which in turn results in a change in the surface potential. Examples of minerals which behave in this fashion are montmorillonite and vermiculite.

When k is altered in colloids with variable charge surfaces, either surface charge or surface potential can be altered. Soil minerals which behave in this manner are the crystalline and non-crystalline oxides and hydrous oxides of iron, aluminum, titanium, manganese and silicon, as well as non-crystalline alumino-silicates. Minerals which behave in this way have also been called colloids with constant-potential surfaces.

In oxide systems, the surface potential Φ_o is related to the hydrogen ion concentration H^+, by the expression

$$\Phi_o = \frac{RT}{F} \ln \frac{H^+}{(H^+)_o} \tag{2}$$

where R is the gas constant, T is the absolute temperature, F is the Faraday constant, and $(H^+)_o$ is the hydrogen ion concentration at the isoelectric point of the colloid. When a soil contains a mixture of oxides, each with its own isoelectric point, $(H^+)_o$ is the hydrogen ion concentration at the zero point of charge. When H^+ is equal to $(H^+)_o$ the surface potential is zero.

Equation 1 can be combined with equation 2 to give,

$$\sigma = \frac{KD}{4\pi} \cdot \frac{RT}{F} \ln \frac{H^+}{(H^+)_o} \tag{3}$$

which relates surface charge σ, to the hydrogen ion concentration H^+ of the soil solution. Minerals which can be described by equation 3 are commonly called colloids with pH-dependent charge. These are the minerals which require special attention in tropical soils research.

BEHAVIOR OF SOILS WITH VARIABLE CHARGE COLLOIDS

There are three soil management parameters in equation 3. They are k, which can be controlled by manipulating the electrolyte concentration of the soil solution, H^+, which is routinely adjusted in liming operations, and $(H^+)_o$, which is often and unintentionally altered when lime, fertilizer or organic matter is added to or depleted from a soil.

The relationship between the surface charge σ and k, H^+ and $(H^+)_o$ is shown in figure 1. Note that σ can take on negative, zero or positive values. Pure goethite and hematite, for example, possess net positive

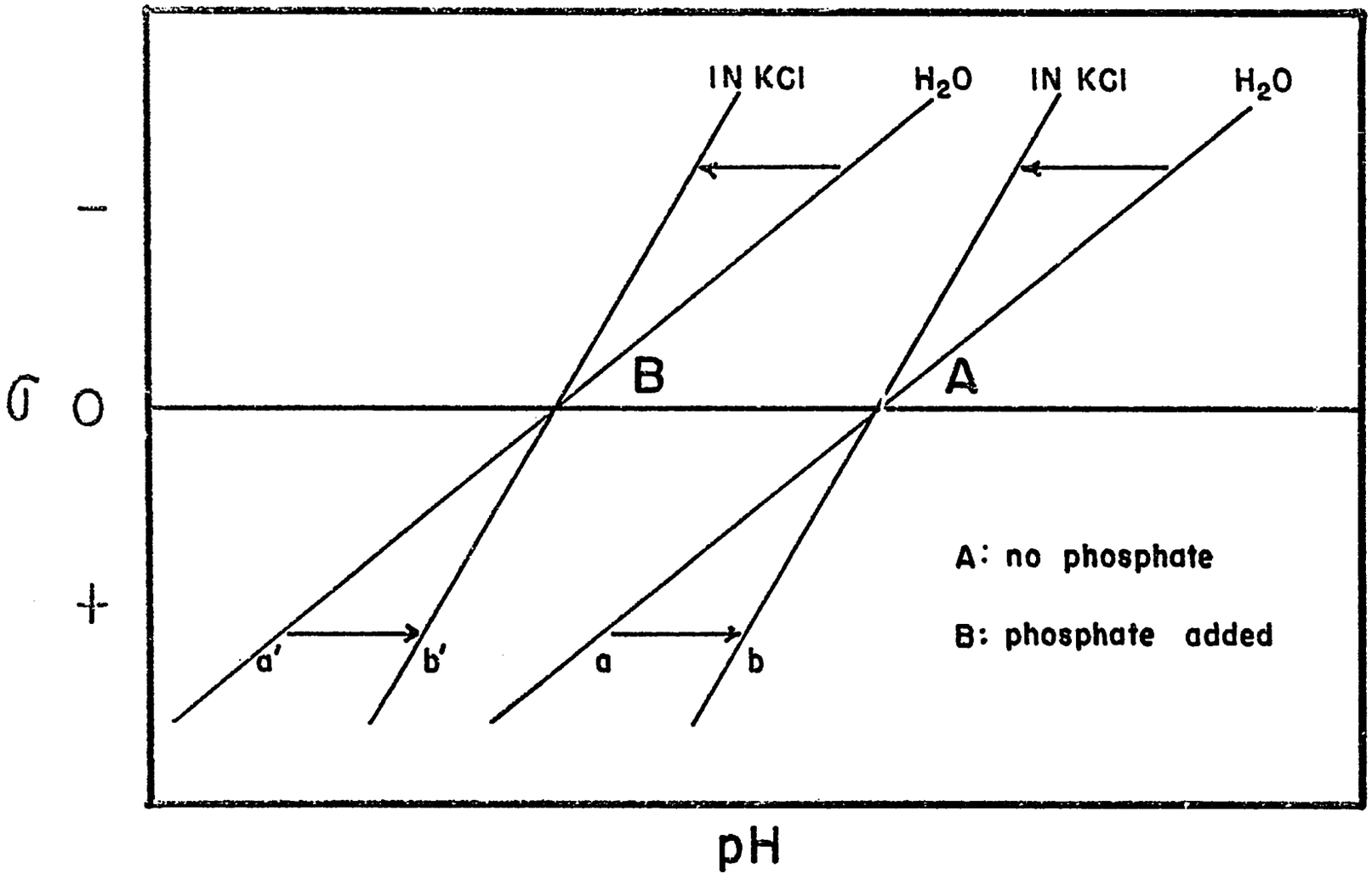

Fig. 1. The dependence of surface charge σ on pH, indifferent electrolyte (KCl) concentration and specific adsorption of phosphate in an oxide.

charge at solution pH values less than 7.0 (Parks and de Bruyn, 1962; Atkinson, et al., 1967). If the pH-dependent charge of a pure oxide is measured in water, curve a is the result, and curve b is the result when NKCl is substituted for water.

When the colloid has net positive charge, the pH is greater in NKCl than in water, if surface charge density is constant. The opposite is true when the surface charge is negative. Mekaru and Uehara (1972) have suggested that the sign of the electrical charge on a soil can be determined by obtaining a delta pH (ΔpH) value which they defined as

$$\Delta pH = pH_{KCl} - pH_{H_2O}$$

where pH_{KCl} refers to the soil pH measured in NKCl, and pH_{H_2O} refers to the pH measured in water. The sign of the ΔpH value corresponds to the sign of the electrical charge on the colloid.

It is often helpful to know the sign of the electrical charge on a soil colloid. Nitrate adsorption and rapid potassium leaching; two situations which rarely occur in soils of the temperate regions are not uncommon in the tropics. One can expect rapid potassium leaching or strong nitrate retention in soils with net positively charged colloids.

Rheology and the physics of transport processes are largely controlled by the sign and magnitude of the charge on the colloid surface. Soils with low net charge are difficult to disperse and possess excellent physical properties in the field. Salts and fertilizers can be leached from them with relative ease due to their low ion adsorption capacity and open structure. The physics of tropical soils is undoubtedly related to their variable charge colloid content.

If one wishes to determine the sign of the charge, the ΔpH value must be obtained with an indifferent electrolyte such as KCl or KNO_3. Electrolytes which contain divalent ions such as $CaCl_2$ or K_2SO_4 can shift the zero point of charge and give erroneous results.

The hydrogen ion concentrations at the zero point of charge $(H^+)_o$ is the third management parameter which can be controlled by man. When phosphorus or other anionic chemicals are added to a soil with variable charge colloids, the adsorbed ("fixed") anion shifts the zero point of charge to lower pH values. This is indicated in figure 1 by the shift in the zero point of charge from point A to B. At any pH between A and B, the soil treated with phosphorus should have a higher net negative charge than one which has not been treated with phosphorus.

Mekaru and Uehara (1972) were able to increase the cation exchange capacity of a Hydrandept (Hilo series) from an initial value of 28 to a high of 127 m.e. per 100 grams by addition of a phosphate salt. Each millimole of adsorbed phosphate increased cation exchange capacity by 0.8 m.e. Phosphorus application has a strong amendment effect on tropical soils.

This increase in net negative charge explains the results obtained by Ayers and Hagihara (1953) who showed that potassium applied as the chloride leached rapidly from a soil, but leaching was markedly reduced when potassium was applied in the form of a phosphate salt. Ayers and Hagihara used a Hydrandept in their study. Similar results have been obtained by Syed-Fadzil (1972) working with a Gibbsihumox and a Eutrandept.

Addition of phosphate or silicate as salts of monovalent cations results in a measurable increase in cation exchange capacity. Monovalent cations are not specifically adsorbed on colloid surfaces and remain as

exchangeable ions. Divalent cations, particularly calcium ions, on the other hand, are adsorbed in the inner Helmholtz layer and are "fixed" on the colloid surface through covalent forces. Liming of tropical soils with calcium carbonate can cause a reduction in cation exchange capacity as shown by Mikami and Kimura (1964). The data in tables 2, 3 and 4 are reproduced from their report.

Mikami and Kimura selected a range of soils for their study. The soils included were two Hydrandepts (Akaka and Hilo series), a Torrox (Molokai series), a Chromustert (Lualualei series), and two Tropohumults (Lolekaa and Manana series). Lime fixation occurred only in the soils with high amounts of oxides and hydrous oxide of iron and aluminum.

When $CaCO_3$ is added to a soil with net positive charge, as was the case in Mikami and Kimura's work, the sign of the charge is reversed by increasing OH^-. This negative charge is effectively neutralized by specifically adsorbed calcium ions. The cation exchange capacity measured by standard procedures at pH 7 was lower in the limed than in the unlimed soil.

The combined effects of specific anion and cation adsorption on cation exchange capacity is found in the work by Rixon (1966). In a long term liming experiment on a Hydrandept (Akaka series) Rixon reported an increase in cation exchange capacity with phosphate application when no lime was added. At the highest lime rate (34,000 lbs/acre), increasing phosphorus application was associated with decreasing cation exchange capacity and decreasing N NH_4OAc extractable calcium. Table 5 contains data from Rixon's work.

Table 2. Net charge of four representative Hawaiian Soils*

Soil	pH in water	pH in 1 N KCl	ΔpH	Mineralogy
Akaka	5.38	5.53	+0.15	hydrated oxides
Hilo	6.02	6.04	+0.02	hydrated oxides
Molokai	6.39	6.04	-0.35	kaolinite
Lualualei	7.47	6.42	-1.05	montmorillonite

*Subsoils were used to minimize the effect of organic matter.

Table 3. Effect of time after liming on the cation exchange capacity of three soils.* Values in milliequivalent/100 grams soil

Soil	No Lime	Time after Liming		
		1 month	3 months	5 months
Akaka (Hydrol Humic Latosol)	58.7	51.1	50.9	52.0
Lolekaa (Humic Latosol)	17.6	17.6	13.1	9.7
Manana (Humic Ferruginous Latosol)	23.3	22.2	17.3	16.7

*Subsoils were used to minimize the effect of organic matter.

Table 4. "Fixation" of calcium as a function of time after liming

Soil	Soil Ca, ppm	Added Ca, ppm	Total Ca, ppm	1 month		3 months		5 months	
				Ca re-covered, ppm	% fixed	Ca re-covered, ppm	% fixed	Ca re-covered, ppm	% fixed
Akaka (Hydrol Humic Latosol)	28	2400	2428	2303	5.2	2152	11.4	2178	14.4
Manana (Humic Ferruginous Latosol)	18	800	818	822	-0.5	796	2.7	787	3.8
Lolekaa (Humic Latosol)	128	800	928	856	7.8	814	12.3	841	9.4

Table 5. Cation exchange capacity, pH, and exchangeable calcium for various lime and phosphate levels added to soils of the Akaka series, Pepeekeo plantation, island of Hawaii

Coral, lb/acre	P_2O_5, lb/acre	pH	Cation Exchange Capacity, me/100 gm	Exchangeable Ca, me/100 gm
0	0	5.0	53.9	0.99
0	200	5.4	64.6	1.64
0	400	5.0	68.7	0.72
34,000	0	6.4	68.4	28.44
34,000	200	6.2	67.6	19.72
34,000	400	6.2	66.4	13.42

Source: Rixon (1966)

In the zero level of lime (Table 5) an increase in cation exchange capacity of 14.8 m.e. was measured. This large increase can not be totally attributed to phosphorus application. In a more carefully controlled laboratory study (Mekaru and Uehara, 1972), phosphate increased cation exchange capacity at a rate of approximately 0.8 m.e. for every millimole of phosphorus sorbed.

A careful reading of Ayers and Hagihara's (1953) paper will show that an identical result was obtained by them. They showed that while application of ammonium phosphate to their soil increased potassium retention, calcium phosphate did not.

The fraction of the total applied calcium which is specifically adsorbed may be very large. Mahilum, et al. (1970) could account for only a small fraction of the applied calcium in exchangeable form, and attributed this to leaching losses. Syed-Fadzil (1972) believes that much of the calcium in the experiment of Mahilum, et al. was still in the soil as specifically adsorbed ion at the time of sampling. Syed-Fadzil applied an equivalent of four tons of calcium silicate per acre to a Gibbsihumox and maintained a budget of this calcium. Three months after application he was able to account for only 50 percent of the calcium in the plant and percolate, and as exchangeable calcium in the soil.

There is a strong suggestion that specifically-adsorbed calcium, like phosphorus, can have long lasting residual effects, and may provide adequate calcium to plants even when only trace amounts of exchangeable calcium are measured.

Direct evidences for specific adsorption of divalent cations on oxide surfaces have been reported by Purcell and Sun (1963), working with

titanium oxide and Modi and Fuerstenau (1957) working with aluminum oxide. Syed-Fadzil's (1972) work clearly indicates that specific adsorption of divalent cations is an important phenomenon in some soils.

ORGANIC MATTER

Just as specific adsorption of phosphate or calcium ions can cause a shift in the zero point of charge, so can specific adsorption of organic matter. Most oxides possess zero points of charge at pH values above pH 6.0, and thus should be positively charged below this value. Soils high in oxides, however, possess net negative charge even at pH values near 5.0, particularly in the surface horizon where organic matter is high. In the subsoil where organic matter is lower, positively charged colloids are more likely to occur.

The data in table 6 show how the sign of the ΔpH value changes from negative values in the surface soil to positive values in the subsoil for two Oxisols. Organic matter is without question the most important and common specifically adsorbed material in tropical soils. The mechanism by which organic matter is sorbed on oxide surface has been suggested by Greenland (1971).

SURFACE COATINGS

Non-crystalline hydrous oxides and alumino-silicates need not be present in large quantities to have an effect on soil behavior. High resolution electron microscope work recently conducted at the University of Hawaii shows that non-crystalline materials do not occur as discrete particles but as coatings on other particles. It is reasonable to assume

Table 6. ΔpH and the sign of the electrical charge of the colloids in the Halii (Gibbsihumox) and Nipe (Acrothox) series

Halii					Nipe*				
Depth in inches	Organic carbon (%)	pH_{KCl}	pH_{H_2O}	ΔpH	Depth in inches	Organic carbon (%)	pH_{KCl}	pH_{H_2O}	ΔpH
0-13	2.87	4.54	4.98	-0.39	0-11	6.04	4.3	5.1	-0.8
13-23	1.91	5.07	5.27	-0.20	11-18	2.09	4.4	5.0	-0.6
23-30	1.31	5.28	5.23	0.05	18-28	1.33	4.7	5.0	-0.3
30-44	0.99	5.22	5.00	0.22	28-38	0.86	5.7	5.2	0.5
					38-48	0.72	6.1	5.5	0.6
					48-62	0.56	6.4	5.7	0.7
					62-70	0.19	6.7	5.8	0.9

*Source: Soil Survey Investigation Report No. 12, SCS, USDA in cooperation with Puerto Rico Agr. Expt. Sta.

that the properties of such a system would be more like that of the coating than that of the underlying material. Variable charge colloids can coat constant charge colloids, but the reverse is not likely to occur. Furthermore variable charge colloids are often non-crystalline and can not be detected by x-ray diffraction methods. An important consequence is that the mineralogy of a soil determined by x-ray methods may not always prove useful in predicting soil behavior.

SUMMARY AND CONCLUSION

A fundamental property of a soil mineral is the sign and magnitude of the charge on its surface. In many layered silicates, the sign and magnitude of the electrical charge is constant. In other minerals, surface charge arises from adsorption of potential-determining ions or specific adsorption of impurities. Colloids with variable surface charge are more commonly found in tropical soils than in soils of the temperate regions. Minerals which are commonly found in tropical soils and which behave as variable charge colloids are the crystalline and non-crystalline oxides and hydrous oxides of silicon, aluminum, iron, manganese and titanium. Non-crystalline alumino-silicates also behave as variable charge colloids.

In soils with variable charge minerals, specific adsorption of anions causes the cation exchange capacity to increase, and specific adsorption of cations causes the cation exchange capacity to decrease. For these soils, prediction of soil behavior will be improved if a model based on variable charge colloid is used.

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