AGENCY FOR INTERNATIONAL DEVELOPMENT
WASHINGTON, D. C. 20523

BIBLIOGRAPHIC INPUT SHEET

FOR AID USE ONLY

1. SUBJECT CLASSIFICATION

A. PRIMARY: Agriculture

B. SECONDARY: Soils

2. TITLE AND SUBTITLE

Management implications of soil mineralogy in Latin America

3. AUTHOR(S)

Uehara, Goro; Keng, J. Ching-win

4. DOCUMENT DATE	5. NUMBER OF PAGES	6. ARC NUMBER
1974	21 p.	ARC

7. REFERENCE ORGANIZATION NAME AND ADDRESS

Department of Agronomy and Soil Science, College of Tropical Agriculture, University of Hawaii, Honolulu, Hawaii 98622

8. SUPPLEMENTARY NOTES (Sponsoring Organization, Publishers, Availability)

(Presented at Symposium on Management of Tropical Soils, Cali, Colombia, 1974)

9. ABSTRACT

A description of the properties of soils containing minerals whose surface chemistry is pH-dependent. The tropical black earths (Vertisols), for example, represent soils containing minerals which are predominantly of the permanent charge (smectite) group. On the other extreme, the Oxisols contain minerals whose surface charge density is almost entirely pH-dependent. Vertisols and Oxisols are frequently heavy textured, but the physical and chemical behavior of these extreme mineralogical end members are markedly different. Vertisols are often difficult to use agronomically because of the poor physical condition of the soil, but with Oxisols the limiting agronomic variable is most frequently soil fertility. The Mollisols, Inceptisols, Alfisols, and Ultisols have soil management requirements that are intermediate between Vertisols and Oxisols. Several descriptive equations, including the Gouy-Chapman equation, are employed to characterize soils containing pH-dependent minerals. Variables discussed include the cation exchange capacity, liming and soil pH, subsoil acidity, anion effects on ZPC, reducing leaching losses, variations in organic matter content, effects of deep plowing, soil-water relations, and the redeeming feature of soil structure in infertile acid soils with pH-dependent charge minerals.

10. CONTROL NUMBER

PN-AAC-377

11. PRICE OF DOCUMENT

12. DESCRIPTORS

Classification
Fertility
Latin America
Management
Soil properties
Soil structure

13. PROJECT NUMBER

14. CONTRACT NUMBER

CSD-2833 211(d)

15. TYPE OF DOCUMENT

AID 590-1 (4-74)

CSD-2833 211(d)
PN-AAC-377

Management Implications of Soil Mineralogy in Latin America[1]

G. Uehara and J. Keng[2]

Minerals which commonly occur in soils can be categorized into two distinct groups. The first group includes those minerals in which surface charge density (and therefore cation exchange capacity) is a constant and permanent quantity. The second group of minerals includes those whose surface charge density and the sign of the surface charge are pH-dependent. Most soils contain mixtures of minerals from both groups.

In general, inorganic soils of the temperate regions contain minerals from the first group. Smectite, vermiculite, illite, and chlorite posses permanent, negative surface charge which arises from ion substitution in lattice interior. For soils containing minerals which are predominantly of this group, well-established soil management parameters, based on surface charge, and ion exchange have been developed and applied successfully.

However, as we move from the northern latitudes, where the bulk of soil research has been conducted and tested, to regions near the equator, we discover that minerals from both groups occur with about equal frequency. In the tropics, one can no longer assume that soil minerals will be of the permanent charge type. The tropical Black Earths (Vertisols), for example, represent soils which contain minerals which are predominantly of the permanent charge (smectite) group. On the other extreme, the Oxisols contain minerals whose surface charge density is almost entirely pH-dependent.

Vertisols and Oxisols are frequently heavy textured, but the physical and chemical behavior of these extreme mineralogical end members are markedly

---

[1]Joint contribution of Agronomy Dept., Cornell University, Ithaca, N.Y.; and Dept. of Agronomy and Soil Sci., Univ. of Hawaii, Honolulu, Hawaii.
[2]Visiting Professor and Graduate Student, Cornell Univ., Ithaca, New York.

different. Use of Vertisols is rendered more difficult because of poor soil physical conditions. In Oxisols this is generally not the case and the limiting agronomic variable is most frequently soil fertility. The Mollisols, Inceptisols, Alfisols, and Ultisols have soil management requirements which are intermediate between Vertisols and Oxisols.

In the Soil Taxonomy developed by the United States Department of Agriculture, mineralogy appears in the family level of soil classification. The soil family, which also includes information on soil temperature and texture, is the category which explicitly provides soil management information.

The purpose of this paper is to present a brief summary of the properties of soils containing minerals whose surface chemistry is pH-dependent. In order to characterize soils with these minerals, it is helpful to use several descriptive equations. The first is the Gouy-Chapman equation

$$\sigma_o = \left(\frac{2n\varepsilon kT}{\pi}\right)^{1/2} \sinh \frac{ze\psi_o}{2kT} \qquad (1)$$

in which σ_o is the surface charge density, n is the concentration of the equilibrium solution in number of ions per cm^3, z is the valence of the counter ion, ε is the dielectric constant of the medium, k is the Boltzman constant, T is the absolute temperature, and ψ_o is the surface potential.

For low surface potentials ($\psi_o << 25$ mV), equation 1 reduces to

$$\sigma_o = \frac{K\varepsilon}{4\pi}\psi_o \qquad (2)$$

where K is the reciprocal of the double layer thickness, and depends on salt concentration.

For minerals with permanent charge, such as montmorillonite, addition or removal of salt from the soil solution (change in K) causes a proportionate change in ψ_o since surface charge σ_o (cation exchange capacity) is a fixed value.

For minerals with pH dependent charge, the same variations in salt concentration will bring about changes in σ_o, if surface potential is held constant. Examples of minerals which respond in this manner are the crystalline and non-crystalline oxides and hydrous oxides of iron, aluminum, titanium and manganese, quartz, amorphous silica, kaolinite, halloysite, allophane, and organic matter. For these minerals the potential ψ_o can be held constant by holding pH constant.

The relationship between surface potential ψ_o and hydrogen ion concentration H^+ for these minerals is

$$\psi_o = \frac{RT}{F} \ln \frac{H^+}{H_o^+} \qquad (3)$$

where R is the gas constant, T is absolute temperature, F is the Faraday constant and H_o^+ is the hydrogen ion concentration at which $\psi_o = 0$.

Equation 2 and 3 can be combined to give

$$\sigma_o = \frac{K\epsilon}{4\pi} \cdot \frac{RT}{F} \ln \frac{H^+}{H_o^+} = \frac{K\epsilon}{4\pi} (0.059) \text{ (ZPC-pH)} \qquad (4)$$

where $\log \frac{1}{H_o^+}$ is the pH at the zero point of charge (ZPC). Equation 4 describes the dependence of cation or anion exchange capacity (σ_o) on pH. Figure 1 illustrates how σ_o will vary as K (salt concentration) and pH are changed.

From equation 4 or Figure 1, one can readily see that when $H^+ = H_o^+$ or ZPC = pH, $\sigma_o = 0$. This situation is represented by the intersection

of the σ_o - pH curves. When a soil is at this pH, σ_o and pH are independent of salt concentration.

In some subsoils samples from Oxisols, the pH measured in water and in NKCl is the same. The field pH of such a material is equal to the zero point of charge. This material has low affinity for monovalent ions such as NH_4^+ or Cl^-. Leaching losses of fertilizer can be a serious problem in such situations.

A few ZPC values of soil materials have been measured, and they generally fall between pH 4-5. In most cases the pH at the zero point of charge shifts to higher values in the subsoil.

It follows from equation 3, that if the soil pH is higher than the pH corresponding to the ZPC, the soil material will be net negatively chargely (cation exchanger) and the pH in NKCL will be lower than that in water. The reverse will be true when the soil pH is on the acid side of the ZPC, and the soil is an anion exchanger. When a soil material is an anion exchanger, the pH in NKCL will be higher than the pH in water.

The cation exchange capacity determined with NNH_4OAc at pH 7 is clearly not as useful in soils with pH-dependent charge minerals as it is in other soils. The useful soil management parameter for soils with pH-dependent charge minerals is the ZPC. ZPC's can be determined by a method described by van Raij and Peech (1972). The method involves addition of acid (HCl) or base (NaOH) to soil suspended in 1.0, 0.1, 0.01 and 0.001N NaCl solution. The pH of these suspensions are measured after a prescribed equilibration period and the results are plotted as me of H^+ or OH^- adsorbed per gram of soil as a function of pH. It is not necessary and probably preferable not to wash the sample with acid prior to ZPC analysis as was done by van Raij and Peech.

Figures 2 and 3 show results of this type for a Dark Red Latosol and a Yellowish Red Latosol from the Central Plateau of Brazil. The zero points of charge correspond to the pH's were the titration curves for several electrolyte concentrations intersect. The shift in ZPC to higher pH values with depth is, in part, related to decreasing organic matter content. In most horizons the curves intersect at a common point and a well-defined ZPC is evident. In the surface horizon of the Yellowish Red Latosol and the deepest horizon of the Dark Red Latosol, the curves for the highest electrolyte concentration do not intersect at the common point. This is related to displacement of adsorbed aluminum ions and exposure of surface charge formerly balanced by them. Under acid soil conditions, adsorbed aluminum ions can effectively block negative charge sites.

If a soil is washed free of extractable aluminum with N NaCl, N $CaCl_2$ or N Na_2SO_4 the ZPC shifts to lower pH's (Figure 4). This clearly indicates that strongly adsorbed cations shift the ZPC to higher pH. Strongly adsorbed anions, on the other hand, shifts the ZPC to more acid pH's.

It should be clearly understood that neutral salts can generate charge on oxide surfaces even when the oxide has no permanent charge. A neutral salt which does not affect the ZPC of a material is called an indifferent electrolyte. Sodium and potassium nitrate or chloride are examples of indifferent electrolytes. When NaCl causes the ZPC to shift as in Figure 4, it is doing so by displacing strongly adsorbed aluminum ion and thus exposing permanent charge.

Salts such as $CaCl_2$ and $NaSO_4$, on the other hand, are not indifferent. They will shift the ZPC of oxide systems (Breeuwsma, 1972).

Analyses of pH-dependent charge on soils from the Llanos of Colombia are presented in Figure 5. Quite clearly, the linear plot in Figure 1,

which comes about from the use of equation 4, does not occur in real soils. Fortunately, the experimental σ_o - pH curves are quite linear in the range (pH 4 to 6) which is most common to these soils, so that equation 4 may in fact be more useful than is expected.

CEC of Minerals with pH-dependent Charge

There are two factors which cause low CEC in soils. Low CEC is most commonly associated with coarse textured soils. A low CEC in heavy textured soil is another matter. If CEC of a heavy textured soil is determined at a pH value very near the ZPC of the soil material, the CEC value will be low. If, on the other hand, the pH is adjusted to some value much higher than the ZPC, the CEC will be correspondingly higher. The change in CEC with increasing pH differs among soils depending on texture and mineralogy. The higher the clay content (higher surface area) and the greater the oxide content, the greater will be the increase in CEC for a unit change in pH above the ZPC. For most soils with pH-dependent charge minerals, the increase in CEC per unit change in pH is greater when the pH is far away (on alkaline side) from the ZPC (see Figure 2 to 5). In addition, at a given pH above the zero point of charge, more calcium ions will be adsorbed than sodium or potassium ions (Keng and Uehara, 1973; Tardos and Lyklema, 1969).

It is also clear from equation 1, 2 or 4 that when CEC is determined at a given pH, the charge and therefore CEC will decrease as excess salt is removed, and will decrease even more if the excess salt is removed with a solvent of low dielectric constant such as alcohol (van Raij and Peech, 1972).

Before laboratory ion exchange determinations can be used as soil management parameters, the laboratory method must take into account the effect not only of pH, but the additional effects related to changes in salt concentration and dielectric constant. The method described by van Raij and Peech (1972) for determining net charge on soil colloids is recommended for soils which are known to contain significant amounts of pH-dependent charge minerals.

Liming and Soil pH

In some heavy textured soils, particularly in Oxisols and Ultisols, an inordinate quantity of lime is required to raise soil pH from an initial value near 5 to a final value of 7. In such soils, lime is consumed to develop surface charge. The crystalline and non-crystalline oxides and hydrous oxides of silicon, iron and aluminum can develop very high surface charge densities (Breeuwsma, 1972; Tardos and Lyklema, 1969).

The slopes of the σ_o - pH curves give a good indication of the buffering capacity of a soil. If σ_o is expressed as me/100 gram soil, the slopes will be steeper as percent clay increases. For a given clay content, the slopes will be steeper as the oxide content increases.

Soils with steep σ_o - pH curves and ZPC values below pH 5, generally do not need to be limed above pH 6. As acid tolerant crops are selected or bred for the tropics, it may become possible to grow crops under very acid conditions, but the pH should be maintained at values higher than the ZPC to reduce leaching losses of nutrient cations.

Subsoil Acidity

In Oxisols it is frequently noted that the pH is higher in the subsoil than in the topsoil; yet root development is severely restricted in the subsoil. This is often associated with subsoils high in aluminum, low in calcium, and pH very near or below the zero point of charge. Such a subsoil will adsorb only trace amounts of calcium, magnesium, or potassium because of low negative charge density.

When lime is added and mixed with the topsoil, most of the lime is consumed to create negative charge. The negative charges in turn are balanced by calcium ions at the site of lime applications, so that very little lime moves to the subsoil. Correcting subsoil acidity remains a serious problem in the tropics.

Anion Effects on ZPC

In addition to lime, the other major limiting agronomic factor is phosphorus nutrition. Phosphorus and lime, in some ways, have similar effects on soils. Both increases net negative charge, and precipitates aluminum ions. Lime increases net negative charge by increasing pH, and phosphorus increases net negative charge by lowering the pH corresponding to the ZPC. Each millimole of adsorbed phosphorus increases CEC by about 0.8 m.e. (Mekaru and Uehara, 1972).

Calcium silicates, in some cases, may be superior to calcium carbonate as a liming material. Calcium silicate not only increases pH and adds calcium and soluble silica to the soil, but can also lower the ZPC through anion adsorption effects. In most instances, however, calcium silicate, even when it is the waste product (slag) of industry, is too expensive and frequently not as effective as ordinary limestone.

In any case, lime experiments in Latin America should include calcium silicate as one of the test materials. When possible basic slag from local industry should be tested.

The strong amendment effects of anionic fertilizers, especially phosphate fertilizers, often result in unexpected field results. In high oxide soils, better crop response to phosphorus fertilizer is sometimes obtained when P is broadcast than when it is banded.

Reducing Leaching Losses

It is common practice to apply nitrogen fertilizers in several applications over a period of time. In heavy textured soils with soil pH very near the zero point of charge, it may be practical to apply potassium fertilizer in the same way. While frequent, light applications of fertilizer reduce leaching losses, this practice requires additional labor which may render it uneconomical. Leaching loss of potassium can be reduced by using potassium sulfate. Ayers and Hagihara (1953) showed that while potassium applied as KCl leached rapidly from high oxide soils, leaching was significantly reduced by using the sulfate or phosphate salt of potassium. Strongly adsorbed anions tend to increase net negative charge in soils with pH-dependent charge minerals. Potassium silicate may have the same effect as a slow release potassium fertilizer. The same arguments should apply to magnesium and calcium.

Organic Matter

The shift in ZPC to higher pH in subsoils (see Figures 2 and 3) is partly related to decreasing organic matter content with depth (van Raij and Peech, 1972; Keng and Uehara, 1973). Increasing organic matter content of the

subsoil through increased root proliferation is desirable, but the unfavorable environment of the subsoil makes this difficult.

Even when nitrogen fertilizer is inexpensive and soil physical conditions are ideal, green manures can benefit high oxide soils by increasing cation retention capacity.

Deep Plowing

Soil physical conditions are not major limiting factors in infertile, acid tropical soils, and yet significant yield increases can be obtained through deep tillage. Deep tillage has a pronounced beneficial effect when lime, fertilizer or organic matter is incorporated into the subsoil. The beneficial effect is related more frequently to improved chemical environment and less often to improved soil physical conditions.

The effect of deep plowing with incorporation of nutrient and amendments to the subsoil is most pronounced in dry seasons. Soils which permit deep root proliferation can help a crop weather periods of drought. Subsoil management should be an integral part of the total management program and should be viewed as a means to enlarge the effective rooting volume. Results of planting density and irrigation trials can be expected to be strongly influenced by subsoil conditions.

Soil-Water Relations

The soil-water relation of well-aggregated kaolin-oxide soils can be markedly different from that in soils with permanent charge minerals. Heavy textured kaolin-oxide soils have moisture release curves, which in some respects, resemble those of sandy soils (Sharma and Uehara, 1968).

In aggregated Oxisols for example, water can reside in large inter-aggregate pores and fine intra-aggregate pores. Water in the large pores

move rapidly under gravitational forces, and field capacity is attained at low tensions, generally between 0.1 and 0.15 bars. Field capacity is attained at this low tension because the hydraulic conductivity at this tension is very low, much like that of a sandy soil.

The water in the fine, intra-aggregate pores is, for the most part, immobile and can be extracted only when extremely high tensions (>100 bars) are applied.

From an agronomist's standpoint, the water content-tension relation between zero and two bars is of interest. Water held at tensions much above two bars in aggregated kaolin-oxide soils is limited in availability to plants because of its low mobility (conductivity).

Soil Structure

The redeeming feature of infertile, acid soils with pH-dependent charge minerals is soil structure. The high aggregate stability of these soils has been frequently attributed to the presence of free iron oxide. Recent high resolution electron microscope examination of soils (Jones and Uehara, 1973) shows that coatings of amorphous substance on soil particles, which act as cementing agents, may be another cause of soil aggregation. These amorphous coatings probably play a major role in determining the physical and chemical behavior of soils.

Water dispersible clay in Oxisols attains minimum values in a soil profile at a point corresponding to the depth at which net electric charge on the soil colloid is zero. In equation 4, this is the situation when $\sigma_o = 0$ and ZPC = pH. The percent water dispersible clay increases rapidly on either side of the ZPC. This feature of oxidic soils is clearly shown

in the Nipe series (Acrorthox) of Puerto Rico. The data are reproduced in Table 1. Similar results are suggested from data compiled for soils from the Central Plateau of Brazil (Cline and Buol, 1973).

In Table 1, data on soil depth, organic carbon, pH in NKCl (pH_{KCl}), pH in water (pH_{H_2O}), the difference between these two pH values (ΔpH), and percent water dispersible clay are presented.

The sign of the ΔpH value corresponds to the sign of the net electric charge of the soil material. Note that water dispersible clay contents approach minimum values as the absolute value of ΔpH approaches zero.

In many cases water dispersible clay attains zero value even when ΔpH is near -0.5. This occurs when adsorbed aluminum blocks permanent negative charge sites. NKCl will displace exchangeable aluminum and the computed ΔpH will be negative, but in water or low electrolyte solutions, the net charge is near zero. This is the case in the deepest sample from the Dark Red Latosol (Figure 2). In that sample, the σ_o - pH curve for the highest (1N) salt concentration intersects the other curves on the acid side of the "effective" ZPC. The "effective" ZPC, which determines water dispersible clay content, corresponds to the intersection of the low salt concentration σ_o - pH curves.

Application of lime to oxidic soils can result in flocculation or dispersion depending on whether liming changes "effective" surface charge from positive to zero values (flocculation) or from zero to negative values (dispersion). In general lime does not disperse kaolin-oxide soils because, while lime is an efficient generator of surface charge, it does not necessarily develop "effective" charge (Lyklema, 1968). Calcium (divalent) ions, to some extent, act in the same manner as aluminum (trivalent) ions.

Both are adsorbed on the oxide surface (specific adsorption) and can block negative charge site, but this occurs to a much lesser extent with calcium.

Table 1. Relation between the sign and magnitude of the electrical charge on % water dispersible clay in the Nipe (Acrorthox) soil.

Depth in inches	Organic Carbon (%)	pH_{KCl}	pH_{H_2O}	ΔpH	Water dispersible clay (%)
0-11	6.04	4.3	5.1	-0.8	22
11-18	2.09	4.4	5.0	-0.6	33
18-28	1.33	4.7	5.0	-0.3	37
28-38	0.86	5.7	5.2	+0.5	2
38-48	0.72	6.1	5.5	+0.6	42
48-62	0.56	6.4	5.7	+0.7	32
62-70	0.19	6.7	5.8	+0.9	34

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

LIST OF FIGURES

FIGURE 1. Relationship between surface charge σ_o, salt concentration C, and equilibrium pH for colloids for which H^+ and OH^- are potential determining ions. When σ_o is positive, pH increases with increasing salt concentration ($C_2 > C_2$). The reverse is true when σ_o is negative.

FIGURE 2. Net electric charge of a Dark Red Latosol from the Central Plateau of Brazil as a function of electrolyte (NaCl) concentration and equilibrium pH.

FIGURE 3. Net electric charge of a Yellowish Red Latosol from the Central Plateau of Brazil as a function of electrolyte (NaCl) concentration and equilibrium pH.

FIGURE 4. The effect of removing extractable aluminum with NaCl, $CaCl_2$ or Na_2SO_4 on the net electric charge of a Dark Red Latosol from the Central Plateau of Brazil as a function of electrolyte (NaCl) concentration and pH.

FIGURE 5. Net electric charge of three surface horizons of soils from the Llanos of Columbia as a function of electrolyte (NaCl) concentration and equilibrium pH.

Fig-1.

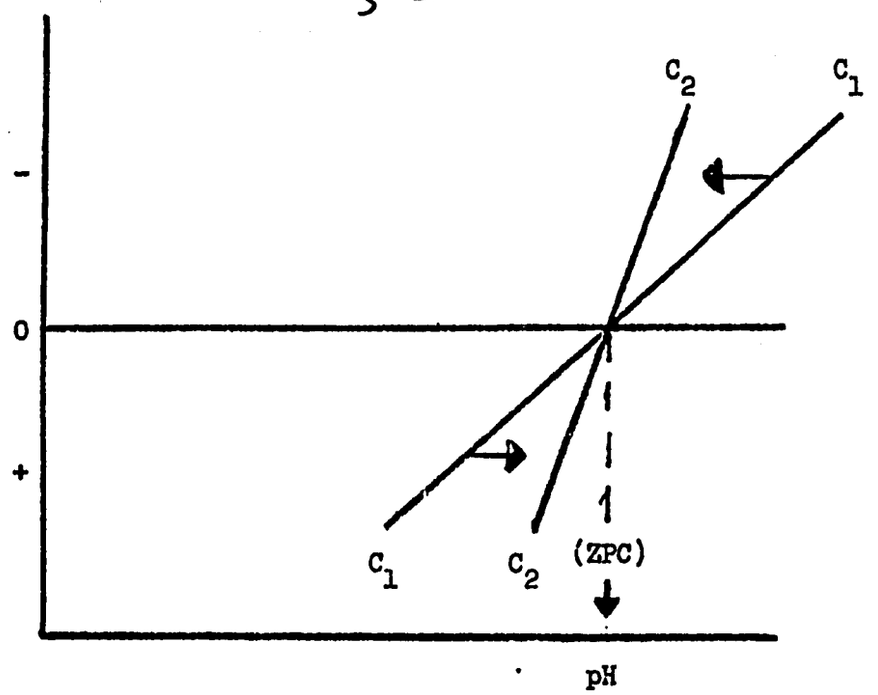


Fig-2-

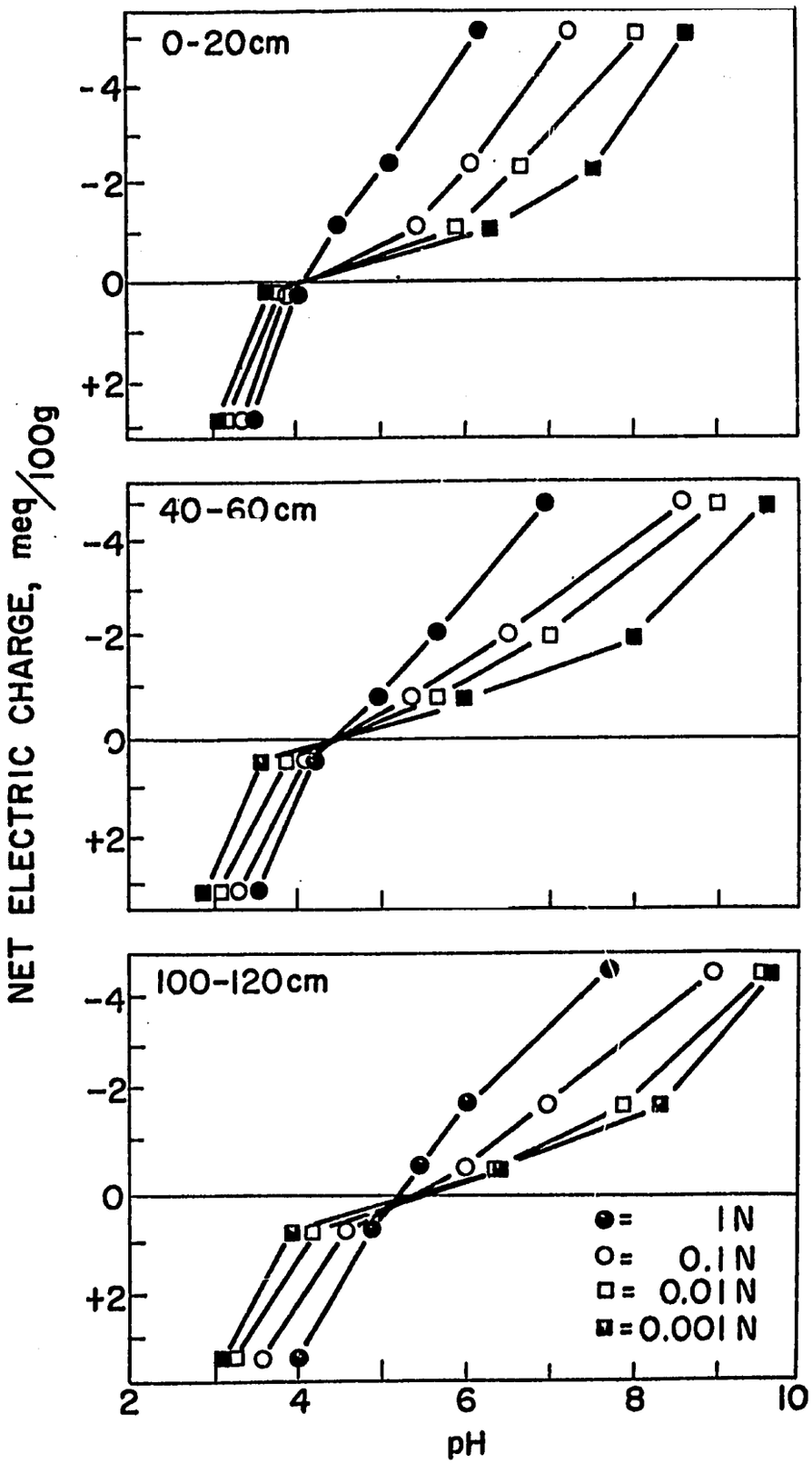

0-20cm
40-60cm
100-120cm
NET ELECTRIC CHARGE, meq/100g
-4
-2
0
+2
2
4
6
8
10
pH
●= 1N
○= 0.1N
□= 0.01N
■=0.001N

FIG. 3

Fig- 3.

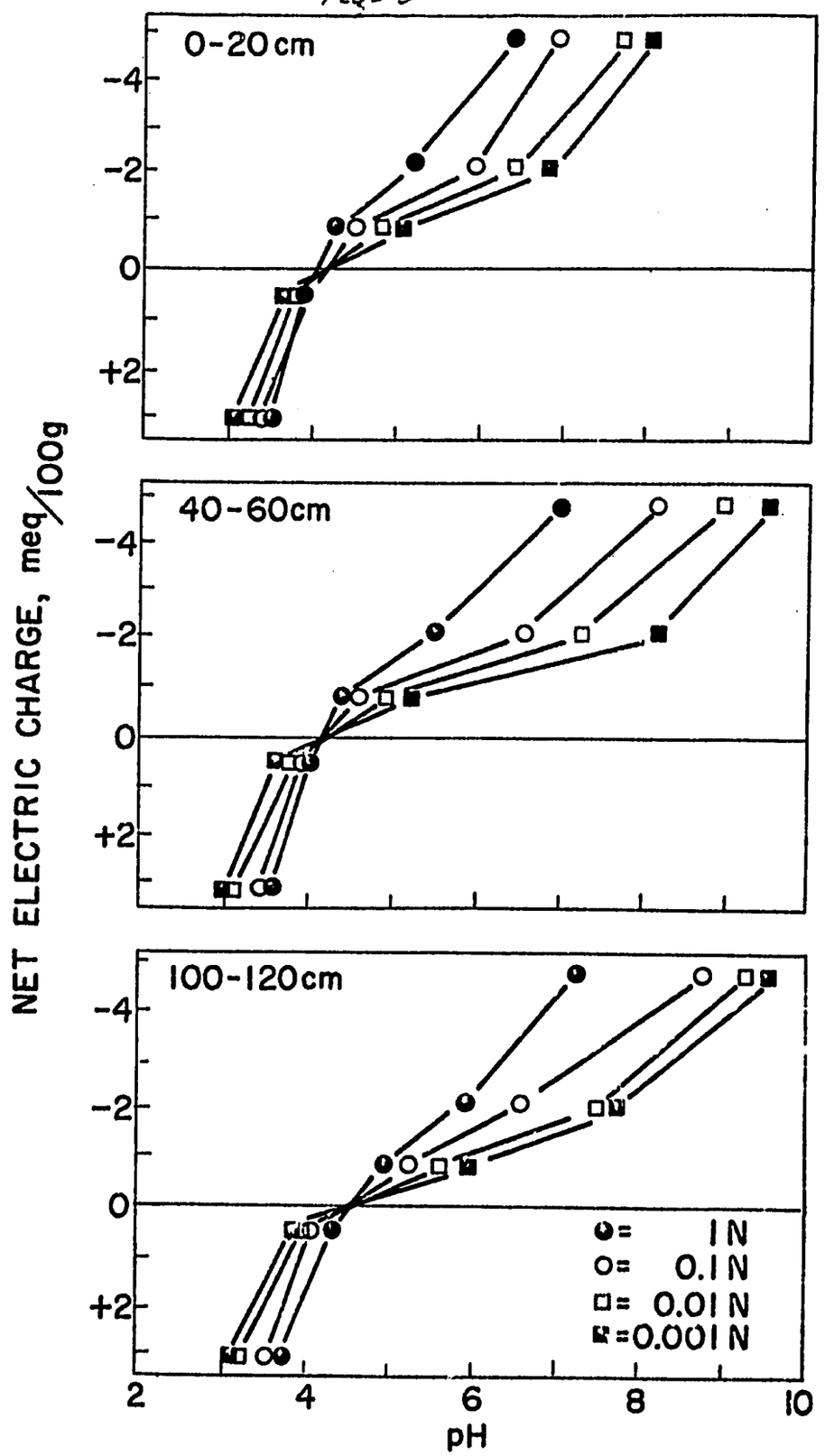

0-20 cm
40-60cm
100-120cm
NET ELECTRIC CHARGE, meq/100g
-4
-2
0
+2
2
4
6
8
10
pH
= 1N
= 0.1N
= 0.01N
=0.001N

Fig. 4

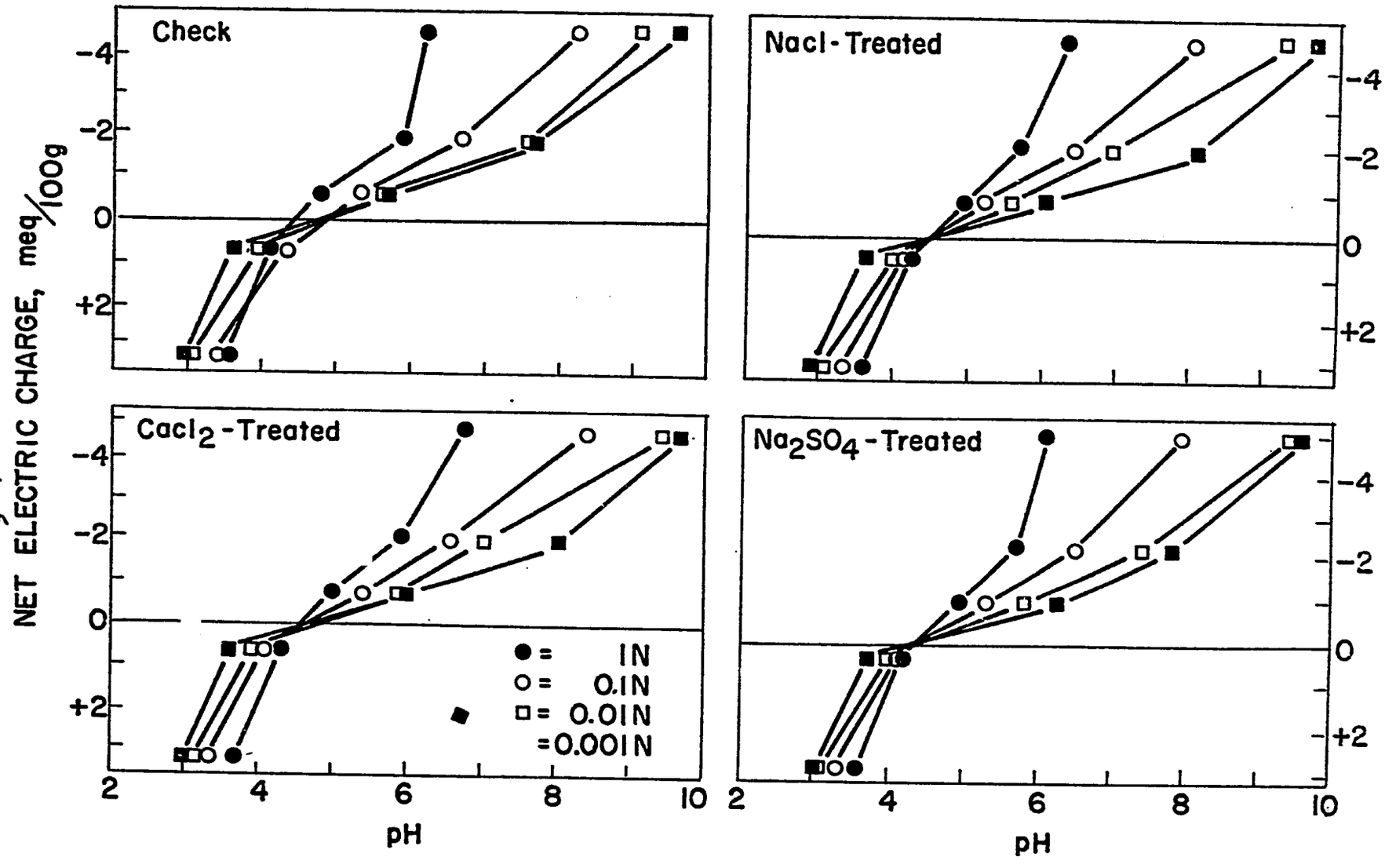
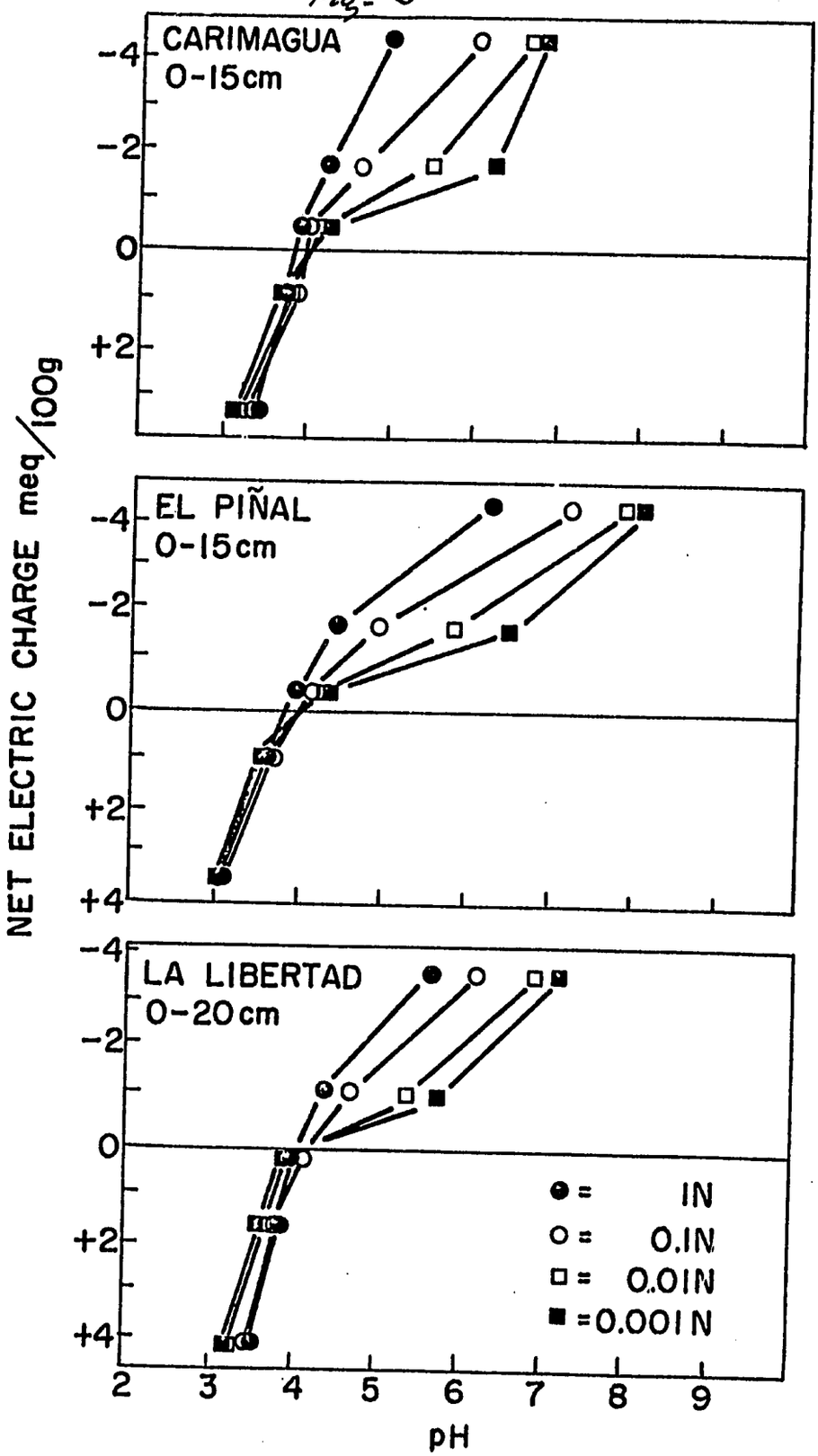

Check
Nacl-Treated
Cacl2-Treated
Na2SO4-Treated
NET ELECTRIC CHARGE, meq/100g
-4
-2
0
+2
2
4
6
8
10
pH
● = 1N
○ = 0.1N
□ = 0.01N
■ = 0.001N

Fig. 5-


CARIMAGUA
0-15cm
EL PIÑAL
0-15cm
LA LIBERTAD
0-20cm
NET ELECTRIC CHARGE meq/100g
pH
-4
-2
0
+2
+4
2
3
4
5
6
7
8
9
● = 1N
○ = 0.1N
□ = 0.01N
■ = 0.001N

LITERATURE CITED

1. Ayers, A. S. and H. H. Hagihara. (1953). Effect of Anion on the Sorption of Potassium by Some Humic and Hydrolhumic Latosols. Soil Sci. 75:7-17.

2. Breeuwsma, A. and J. Lyklema. (1971). Interfacial Electrochemistry of Haematite (α-Fe_2O_3). Dis. Faraday Soc. 52: 324-333.

3. Breeuwsma, A. (1973). Adsorption of Ions on Hematite (α-Fe_2O_3). Ph.D. Thesis, Agricultural Univ., Wageningen, The Netherlands.

4. Cline, M. G. and Buol, S. W. (1973). Soils of the Central Plateau of Brazil. Agronomy Mimeo 73-13. Cornell University.

5. Jones, R. and G. Uehara. (1973). Amorphous Coatings on Mineral Surfaces. SSSAP, submitted for publications.

6. Keng, J. and G. Uehara. (1973). Chemistry, Mineralogy, and Taxonomy of Oxisols and Ultisols. Proceedings of the Florida Soil and Crop Science Society. Vol. 33.

7. Lyklema, J. (1968). The Structure of the Electrical Double Layer on Porous Surfaces. J. Electroanal. Chem. Interf. Electrochem. 18:341-348.

8. Mekaru, T. and G. Uehara. (1972). Anion Adsorption in Ferruginous Tropical Soils. SSSAP, 36:296-300.

9. Sharma, M. L. and G. Uehara. (1968). Influence of Soil Structure on Water Relations in Low Humic Latosols. I. Water Retention. SSSAP, 32:765-770.

10. Sharma, M. L. and G. Uehara. (1968). Influence of Soil Structure on Water Relations in Low Humic Latosols. II. Water Movement. SSSAP. 32:770-774.

11. Tardos, TH.F. and Lyklema, J. (1969). The Electrical Double Layer on Silica in the Presence of Bivalent Counter-Ions. J. Electroanal. Chem. Interf. Electrochem. 22:1-7.

12. Van Raij, B. and M. Peech. (1972). Electrochemical Properties of Some Oxisols and Alfisols of the Tropics. SSSAP 36:587-593.