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Stabilization of Calcium by Surface Charge Variation in an Oxisol[1]

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ABSTRACT

In the surface layer of a Ca-deficient, fine-textured Hawaiian Oxisol, concentrations of Ca in solution were poised against tendencies to increase with liming in the pH-range 5-6, and to decrease with dilution in the range of water content 0.35 to 2.0. Effects of lime and water content on the distribution of Ca between solid phase and solution were shown to be quantitatively consistent with effects of pH and ionic strength on exchange capacity.

Relationships between soil pH, cation exchange capacity, and dissolved Ca were determined in soil samples taken from a field-liming trial. Effects of ionic strength on exchange capacity were determined by summation of adsorbed metal cations after equilibration of soil samples in different salt solutions. Effects of water content on cations in solution were determined by analysis of solutions centrifugally extracted at various water contents.

The results help explain why Ca-deficiency may sometimes be corrected better by neutral Ca salts than by lime and why saturation-extract Ca may approximate soil-solution Ca adequately for diagnostic purposes.

Additional Index Words: **Al, Mg, K, Na, anion and cation exchange stoichiometry, cyclic salt, mass flow, tropical soils**

VARIABILITY OF SURFACE CHARGES has important effects on behavior of ions in highly weathered soils whose colloids are mainly kaolinite, sesquioxides and humus. As soil pH is increased toward neutrality, negative surface charge will increase and positive charge decrease, and as electrolytes in the solution phase become diluted, both positive and negative surface charges will decrease (6, 9, 11, 12, 15, 24). The purpose of this paper is to show that variations in cation exchange capacity help to account for apparent anomalies in behavior of Ca which became evident from a field-liming trial on a fine-textured Hawaiian Oxisol, the Wahiawa silty clay (17, 18, 19).

Although Ca-deficiency is frequently corrected by small applications of limestone, the Wahiawa topsoil required about 5 metric tons $CaCO_3$/ha before Ca in the saturation extract rose substantially above the low value of 0.3 meq/liter (18). This "buffering" of Ca at low levels can be only partially explained by considering cation exchange equilibrium and affinities of adsorption sites for Ca (17).

Further, concentrations of Ca in aqueous extracts varied little with dilution, an effect that has been observed in other acid soils (7, 8, 21). This apparent buffering of Ca against effects of dilution, which has possible diagnostic significance, is also not readily explained in terms of cation exchange alone.

This paper presents measurements of effects of pH and ionic strength on the soil's cation exchange capacity, and shows that these effects are quantitatively consistent with the effects of liming and water content on the distribution of Ca between solid phase and solution.

PROCEDURES

Soil Samples

The soil is a Wahiawa silty clay (Tropeptic Eutrustox) from the University of Hawaii's Poamoho Experimental Farm on the island of Oahu. It is developed on mafic aphanitic rock with possible volcanic ash influence. The samples were taken from the surface 0-15 cm layer, which has about 1.6% organic carbon, and consists mainly of kaolinite and hematite with some goethite, gibbsite, mica, manganese oxide, and amorphous minerals (23)

For the study of effects of pH (lime), a set of samples were taken from several points in a continuous function lime trial described elsewhere (18). A single bulk sample from a point just outside the trial was used for the studies of effects of moisture content on solution composition and effects of ionic strength on CEC.

Effects of pH (lime) on CEC and Adsorbed Ca Fractions (Fig. 1)

Exchangeable cations were extracted from 3-g samples of soil with three successive 30-ml portions of 1*M* NH_4Cl, bulked and analyzed for Al, Ca, Mg, Na, and K. Since exchangeable Na was < 0.1 μeq/g soil, CEC was taken as the sum of exchangeable Al, Ca, Mg, and K.

Effects of Ionic Strength on CEC (Fig. 2)

Samples of 3-g soil were suspended in 200-ml lots of either KCl or $CaCl_2$, at various concentrations, viz. 0.5, 5, and 50 m*M* for KCl, and 0.2, 2, and 20 m*M* for $CaCl_2$. The suspensions were shaken intermittently for 2 days. Then pH was measured in the suspensions and they were centrifuged. The equilibrium solution was decanted for analysis. The wet soil sample was weighed to determine the amount of residual solution, and then extracted with three successive 30-ml portions of 1*M* NH_4Cl. These were bulked

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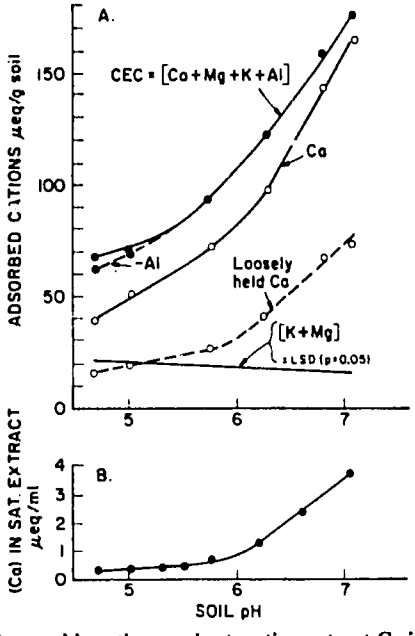

Fig. 1—Exchangeable cations and saturation-extract Ca in relation to changes in pH induced by addition of $CaCO_3$ in the field. "Loosely held Ca" was determined by extraction with dilute KCl (17).

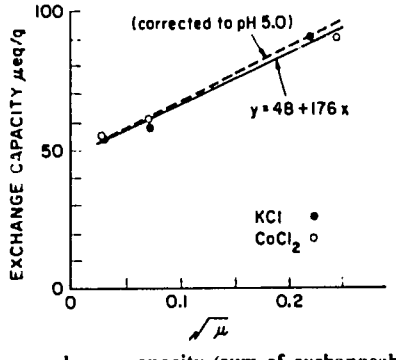

Fig. 2—Cation exchange capacity (sum of exchangeable metal cations) in relation to ionic strength of solution phase (μ), as determined in soil samples suspended in solutions of KCl or $CaCl_2$.

for determination of exchangeable cations, with correction for the cations left in the residual solution from the initial equilibration, error due to negative adsorption being assumed negligible. Values of CEC were taken as the sum of exchangeable Ca, Mg, K, and Al. Ionic strengths of the initial equilibrating solutions were calculated from analytical values for Ca, Mg, and K, assuming other cations to be negligible and anions to be monovalent (i.e., essentially Cl).

Effects of Moisture Content on Solution-phase Cations (Fig. 3.)

Several samples were made up to various water contents (with addition of toluene to suppress microbial activity), equilibrated, and then centrifuged at just sufficient speed to separate about 3 ml clear solution from each sample. For values of θ equal to 2, 1, and 0.8, the soil sample sizes were, respectively, 10, 15, and 20 g, the equilibration time was 18 hours, and the centrifuge was run for 5 min at low speed. For values of θ equal to 0.6 and 0.4, the sample was 100 g, equilibration time 3 days, centrifugation time 40 min (refrigerated at 25°C), and the speed sufficient to give relative centrifugal force at the bottom of the sample equal to 160 for θ = 0.6 and 4,000 for θ = 0.4. (The 100-g samples were extracted in stainless steel centrifuge cups fitted with acrylic castings to support the

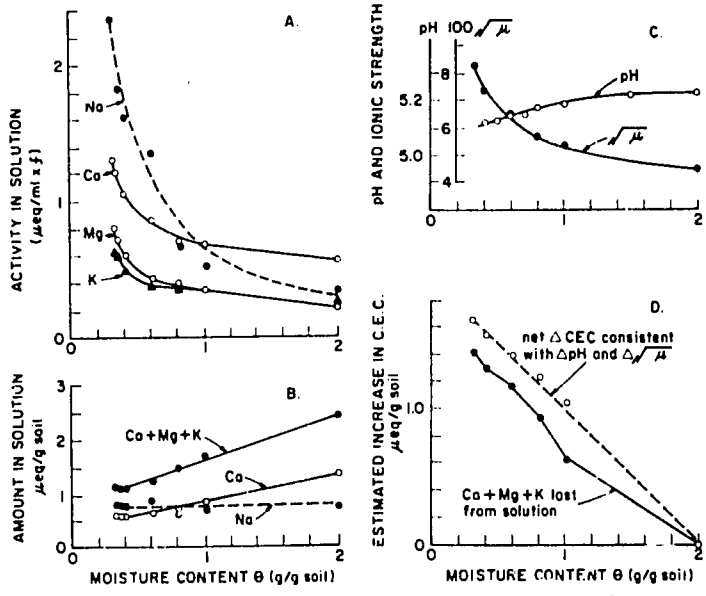

Fig. 3—Effects of variation in moisture content θ, on: *(A)* cation activites in centrifugally extracted solution phase, (f = calculated activity coefficient: Na data fitted by curve (Na) = 0.7/θ), *(B)* estimated cation contents in solution, per gram of soil, *(C)* soil pH and estimated ionic strength of solution phase, and *(D)* changes in cation exchange capacity; comparison of estimates from removal of cations from solution with estimates from shifts in pH and ionic strength.

sample and collect the effluent (K. R. Helyar, unpublished).) The samples at θ = 0.4 were then further centrifuged (at 1-day intervals) at higher RCF, viz. 13,000 and 21,000, to release solution extracts corresponding, respectively, to θ values of 0.37 and 0.35. The centrifuge could not remove water from this soil at $\theta < 0.35$, nor can plants. At this point the soil moisture retention curve flattens, reflecting a discontinuity between interaggregate voids and much smaller intraggregate voids which require extremely high forces to empty (22). Since centrifugal extraction emptied only large pores, salt sieving and Donnan effects probably had little influence on the cationic composition of the extracted solutions. Extracted solutions were analyzed for Ca, Mg, Na, and K. Ionic strengths were calculated (Fig. 3C), again assuming other cations to be negligible and anions to be monovalent. Activity coefficients were calculated using extended Debye-Hückel coefficients presented by Adams (1, 2). Soil paste pH was determined (Fig. 3C), at θ down to 0.4, by averaging readings from 10 separate insertions of a glass electrode, well separated from the reference electrode to minimize salt-effects from the liquid junction.

Analytical Procedures

Aluminum was determined by colorimetric assay of the 8-quinolinol complex extracted into chloroform (10). Other cations were determined by atomic absorption spectrometry after addition of $LaCl_3$ and HCl.

RESULTS AND DISCUSSION

Effects of $CaCO_3$

Figure 1 shows how exchangeable cations, exchange capacity, and Ca in the saturation extract related to soil pH as affected by liming. Exchangeable Al declined from low initial values to essentially zero at pH 5. Exchangeable K and Mg declined slightly with increasing lime, possibly because of displacement and leaching during the 4 months between liming and sampling.

The CEC (sum of exchangeable cations) increased three-

fold, from 65 to 175 μeq/g soil, as the pH increased from 4.8 to 7.1. This additional charge, being almost precisely equivalent to the amount of $CaCO_3$ reacted, helped to keep dissolved Ca low. The form of the charge/pH curve is consistent with curves determined over a wider range of pH by others (9, 12, 15). Extrapolation to pH 4 yields an estimate of permanent charge of about 50 μeq/g, consistent with the likely contribution from kaolinite and mica.

The additional CEC was occupied by Ca. Some of the exchangeable Ca was in a loosely adsorbed form, easily displaced by dilute KCl (17). Both this fraction and the Ca in the saturation extract increased little as pH was raised from 4.8 to 5.8, but increased sharply as pH was further raised from 5.8 to 7.1 (Fig. 1). In part, this agrees with evidence that Ca is held loosely against hydrolytic displacement from pH-dependent sites on silicate clays (5,14). However, charge sites on humus are probably important here, and some of the Ca on pH-dependent sites is evidently held strongly (17, and Fig. 1).

Effects of Ionic Strength (μ)

Figure 2 shows effects of varying concentrations of KCl and $CaCl_2$ on CEC. The curve appropriately implies existence of about 50 μeq/g permanent charge, at $\mu = 0$, and an increase in CEC with increasing μ (6, 9, 11, 12, 15).

Effects of Soil Water Content, θ

Figures 3A and 3B show effects of θ on solution-phase cations. A simple model of soil with fixed surface charge would predict that total cations per gram of soil would remain constant, and that total concentration in solution would increase reciprocally as θ decreased. This was not true, except for the individual cation Na.

The soil adsorbs Na weakly. This would be expected where much of the charge is pH-dependent and Ca is the main complementary cation (14). Exchangeable Na was < 0.2 μeq/g soil, although Na was a major constituent of the soil solution, where it is probably maintained by inputs of cyclic salt. Because Na was essentially not adsorbed, total Na in solution remained constant as θ decreased (Fig. 3B) and Na concentration rose sharply (Fig. 3A).

By contrast, Ca, Mg, and K concentrations increased little with decreasing θ (Fig. 3A), and their total content in solution, per gram of soil, decreased (Fig. 3B). The partial removal of these cations from the solution can be viewed as a buffering of their concentrations against the effect of decreasing θ. The removal is unlikely to be due to precipitation, because Ca, Mg, and K have no salts sufficiently insoluble to precipitate from such dilute acid solutions as these. On the other hand, increased sorption of Ca, Mg, and K, implying increase in charge with decrease in θ, can be justified.

The surface charge of variable-charge ("constant-potential") colloids is a function of pH and ionic strength. Theoretical formulations of these relationships have been presented (e.g., 6, 9, 12, 24). Although these formulations cannot be applied with precision to soils containing ill-defined mixtures of colloids, they suggest that the system can be approximately described by the following simplified model:

$$\mathrm{CEC} = f(\mathrm{pH} \times \mu)$$
$$\log \mathrm{CEC} = A + B \log \mathrm{pH} + C \log \mu,$$

where A, B, and C are arbitrary coefficients.

For calculating changes in CEC the coefficient A is of no concern. Coefficient B was estimated by regression from the data of Fig. 1A, and C was estimated graphically from the data of Fig. 2. Corrections were applied to take account of the small variation of ionic strength associated with increase in pH in Fig. 1, and the small variation in pH associated with increase in μ in Fig. 2. For simplicity, B and C were taken as constants within the appropriate limited ranges over which pH and μ varied with change in moisture content (Fig. 3C). The coefficients had values of 4.6 and 1.5 for B and C, respectively. As the moisture content decreased, the drop in pH (Fig. 3C) should have tended to decrease CEC and the rise in μ (Fig. 3C) should have tended to increase CEC.

Figure 3D shows the calculated net increase in CEC as θ decreased from 2 to 0.37; and compares this with the observed decrease in the content of dissolved cations per gram of soil, replotted from Fig. 3B. The variation in CEC is small in relation to the CEC itself (about 1.5 μeq/g in 60 μeq/g), but it is enough to account for the shift in dissolved cation content and the buffering of dissolved cation concentrations.

Stoichiometric Considerations

Variation in CEC requires explanation of the stoichiometric changes in solution and in the interface. The observed shifts in pH (Fig. 1, Fig. 3C) represent quantities of free hydrogen ion in solution that are negligible in comparison with the changes in other solution cations and in CEC. Two processes may help to account for stoichiometry when CEC increases with increased pH or decreased θ. They are: (i) association and dissociation of weak acids in solution, and (ii) variation in anion exchange capacity (AEC), which occurs simultaneously with variation in CEC when pH or salt concentration is altered (6, 9, 11, 12, 15, 24).

Liming presumably increased CEC by causing release of surface protons which reacted with carbonate to produce CO_2 and water. Calculated increase in bicarbonate accounts for only 2% of the increase in solution Ca, if atmospheric equilibration is assumed. More bicarbonate would of course form if the soil air was enriched in CO_2. Anions from soluble organic acids should also increase with pH. But, neither bicarbonate nor organic anions may be abundant because the soil has little microbial activity, as indicated by extremely slow rates of N mineralization (18). On the other hand, liming could release ample amounts of adsorbed anions, since AEC in highly weathered soils can decrease markedly with increase in pH in the range 4 to 7 (9, 11, 15). (This decrease in positive charge could also enhance the strength of adsorption of Ca and contribute to the observed buffering of Ca in solution in the pH range 4.8 to 5.8.)

When θ was increased, increases in bicarbonate and dissociated organic anions were again probably minor in relation to the shift in CEC; but significant amounts of adsorbed anions may have been released because decrease in salt concentration would decrease AEC as well as CEC. This may be viewed as simultaneous neutralization of a negative sur-

face charge site by adsorption of a proton and neutralization of a positive site by a hydroxyl, resulting in "desorption of salt" and little change in pH.

Agronomic Implications

The data suggest that analysis of Ca in the saturation extract may be a useful simple test for Ca-fertility. It approximated the concentration in solution in the field moisture range with no > 30% error (Fig. 3A). This correspondence is not unusual in acid soils (7, 8, 21), and accounts for observed relationships between saturation-extract Ca and plant growth (18). Diagnostic interpreta ion of solution Ca data would be impaired if Ca were to become concentrated at the root surface by convective mass flow; but this accumulation is unlikely at deficient or nearly deficient concentrations, which for many plants of interest are around 1 meq/liter (4, 13, 16). For a high-Ca legume operating at 1 meq/liter in the soil solution, it can be estimated (4, 20) that convective flow is likely to approximate plant uptake, so that growth should relate to saturation-extract Ca much as it relates to concentrations of Ca in solution culture. At Ca concentrations much below 1 meq/liter, convective flow of Ca should fall short of uptake. Saturation-extract Ca would then estimate the concentration of Ca at the outer boundary of an inward diffusion gradient, and thus tend to underestimate intensity of deficiency on markedly deficient soils. This minor fault would be minimized by calibration of the test in the field.

Correction of Ca-deficiency requires little $CaCO_3$ in some soils (16). However, in soils like the Wahiawa, Ca-sensitive crops may need large, expensive lime applications to correct Ca deficiency, more than they need for correction of acidity or Al or Mn toxicity. Efficiency could be gained by selecting crops with low Ca-requirement and by using just enough lime to correct acidity (with supplementary Ca provided by neutral salts which raise CEC less than carbonates do). These suggestions agree with practical experience in Hawaii, where the most important crops, sugar cane (*Saccharum officinarum* L.) and pineapple (*Ananas comosus*), are low-Ca crops and where gypsum has been recommended as a source of Ca (3).

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