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EFFECT OF pH AND DISSOLUTION TREATMENT
ON THE K/Ca EXCHANGE SELECTIVITY OF
SOME ULTISOLS AND OXISOLS

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16. Abstracts K/Ca cation exchange selectivity (CES) values were determined at pH 5 and pH 7 on surface and subsurface horizons of three Ultisols and Oxisols from Colombia and Puerto Rico. The CES values were also determined following treatments for the removal of organic matter, and interlayer Al-hydroxy polymers of the chloritized expandable layer silicates present in the clay fractions of the soils. The CES values were dependent upon the pH and the treatment, and in general were greater at pH 5 than at pH 7 for any treatment. Thus the pH dependent cation exchange capacity of these soils appeared to be selective for the adsorption of calcium over potassium. The CES values increased markedly at pH 5 or at pH 7 following the removal of organic matter or interlayer Al-hydroxy polymers. The large increase in potassium selectivity upon the removal of organic matter was attributed to the removal of organic molecules that were sterically or electrostatically blocking the selective potassium adsorption sites of expandable 2:1 silicates.					
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Effects of pH and Dissolution Treatment on the K/Ca Exchange
Selectivity of Some Ultisols and Oxisols

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INTRODUCTION

The selective absorption of potassium by weathered micaeous, vermiculitic clay minerals has been a subject of interest to soil scientists for the past two decades (Wiklander, 1950; Bolt *et al.*, 1963; Jackson, 1963). The majority of these studies have been confined to soils of temperate climatic regions that contain substantial amounts of weathered micaceous, vermiculitic clay minerals.

Potassium selectivity studies on highly weathered soils of the humid tropics are few in number, largely because these soils are considered to be entirely devoid of the vermiculitic type clay minerals that are considered to be specific for the absorption of potassium. However, recent results on the clay mineralogy of some Oxisols and Ultisols of Puerto Rico and Colombia (Weaver, 1973a, 1973b) as well as those from Latin America and Africa (Oliveira *et al.*, 1971; LeRoux, 1973) have shown that these soils may contain small amounts of mica and vermiculite.

To a large extent the study of potassium has been of secondary interest on these soils in comparison to phosphorus and acidity. However, with intensive cultivation of these soils and elimination of P and acidity problems, it is quite likely that potassium may become a limiting factor. Accordingly, knowledge is going to be needed on the mineralogical composition and its

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influence on the behavior of potassium in these soils.

Therefore it was the objectives of this research to determine the K/Ca selectivity of several Oxisols and Ultisols which have been well characterized mineralogically. In addition, because the ion exchange complex of many of the highly weathered soils of the humid tropics is dominated by materials that have a pH dependent charge, i.e., organic matter, hydrous oxides of iron and aluminum, 1:1 layer silicates, it was also decided to determine the influence of pH on the potassium-calcium exchange selectivity.

MATERIALS AND METHODS

Two Oxisols and an Ultisol were selected for study. The mineralogy of the clay size fraction of the surface horizons of these soils on an iron-free basis as determined by the methods of Alexiades and Jackson (1966) is given in Table 1. The Humatas series of Puerto Rico (Typic Tropohumult) contained the largest amount of mica and vermiculite as indicated by total K_2O and K-fixation. The Oxisol from Puerto Rico, the Catalina series (Tropoepitic Haplorthox) had the smallest amount of mica and vermiculite, while the other Oxisol, the Carimauga, a Typic Haplustox from the Eastern Plains of Columbia was intermediate between the Humatas and Catalina. The Carimauga soil was also noted by X-ray diffraction (XRD) results to contain a small amount of pyrophyllite, approximately 5-10% which is not listed in Table 1. While mica, vermiculite, and Al-chlorites are reported as separate entities in the table, XRD results suggested that they occurred together as mixed layer species. This can be seen in the XRD patterns (Fig. 1) of the Carimauga soil clay-sized fraction before and after treatment to remove Al-hydroxy

interlayers of pedogenic Al-chlorite. In the untreated sample, in addition to basal reflections of kaolinite, there is a pronounced peak at 14 \AA for Al-chlorite, that collapsed to a broad peak at 10 \AA after heating the K-saturated sample at 550°C . After the removal of hydroxy-Al interlayers, by heating at 400°C followed by boiling 0.5 N NaOH extraction, the 14 \AA peak was replaced by a broad peak at approximately 12 \AA with Mg-saturation. With glycerol solvation, the basal spacing of the peak did not change much, but there was a decrease of intensity probably as a result of excess glycerol. With K-saturation, the peak largely collapsed to 10 \AA , and collapse was complete after heating the K-saturated sample at 350°C . Similar X-ray diffraction patterns were obtained for the Humatas and Catalina soil clays from Puerto Rico. Probably in these soils mica has weathered to vermiculite by K-depletion and lowering of layer charge and then the precipitation of Al-hydroxy polymers for form zones or layers of Al-chlorite.

The K/Ca selectivity numbers were determined on air-dried, less than 2 mm samples in a manner similar to that described by Dolcater *et al.* (1968). Briefly, this method consisted of equilibration of a sodium saturated sample with a mixed solution which was 0.005 N with respect to K and Ca. The absorbed K and Ca were displaced by repeated centrifuge washings with $\text{Mg}(\text{OAc})_2$ solution. Excess salts were not washed out prior to displacement, but were taken into account by determination of the weight of the excess salt solution. The pH was controlled at pH 5 or pH 7 by initially equilibrating the samples with Na-acetate buffer solutions. The K/Ca selectivity numbers were determined on: (1) Untreated samples; (2) samples that had been treated for the removal of organic matter by the use of sodium hypochlorite adjusted to pH 9.5 (Lavkulich and Wiens, 1970); and (3) samples that had been treated

for the removal of hydroxy-Al interlayers by heating the samples at 400°C followed by extraction with boiling 0.5 N NaOH (Dixon and Jackson, 1962).

RESULTS AND DISCUSSION

For the untreated samples, the K/Ca selectivity values (Fig. 2) ranged from 0.15 to 0.24. These values are intermediate between those reported by Dolcater et al. (1968) for montmorillonite which is not selective for K and vermiculite which selectively absorb K and apparently reflect the small amount of vermiculite in these soils. There was a substantial amount of pH dependent CEC in these soils, the CEC being taken as the sum of exchangeable K^+ and Ca^{2+} . This pH dependent CEC appeared to have an influence upon the K/Ca selectivity numbers. This is, as the pH was increased from 5 to 7, the K/Ca selectivity numbers decreased. This is an indication that the pH dependent CEC is selective for Ca over K. This would seem plausible when it is realized that the pH dependent CEC arises from various sources, such as organic matter, hydrous oxides of iron and aluminum, and broken bonds at the edges of clay minerals. These charges are of a nature such that they are nonspecific for the sorption of potassium, and it is generally considered that for such charge sites that divalent cations such as Ca^{2+} are more strongly and therefore selectively adsorbed over monovalent cations such as K^+ .

The results (Fig. 3) for the samples that had been treated for the removal of organic matter displayed a substantial reduction in the amount of pH dependent CEC. There was, however, a small amount of pH dependent CEC remaining, probably as a result of the presence of hydrous iron and aluminum

oxides and edge charges. Again, as with the untreated samples, the pH dependent charge component appeared to be selective for Ca over K^+ . The most noticeable effect, however, of the organic matter removal, was the very large increase in potassium selectivity. That is, the K/Ca exchange selectivity numbers ranged from 0.55 to 0.67 as compared to 0.15 to 0.24 of the untreated samples. In part, this increase could be a reflection of the concentration of K-selective sites, as a result of the removal of organic materials which are not specific for the absorption of K. However, this would not entirely explain the increase in K-selectivity inasmuch as there was an increase in the amount of potassium sorbed and a decrease in calcium sorbed in comparison to the untreated samples.

The removal of the hydroxy-Al interlayers caused a large increase in the CEC (Fig. 4) as a result of the unblocking of permanent, isomorphous substitutional charge. There still remained a small amount of pH-dependent CEC probably due to broken bonds at the edges of layer silicates. Again the pH dependent CEC was selective for Ca^{2+} over K^+ . The K/Ca selectivity numbers indicated that the K^+ selectivity was much larger than that of the untreated samples, but in general were slightly less than those of the samples that were free of organic matter.

In summary, it can be said: (1) the pH dependent CEC was selective for Ca over K, and (2) removal of organic matter and/or Al-hydroxy polymers increased K-selectivity over that of Ca. The reason for the removal of organic matter causing the larger increase in K-selectivity is probably due to organic materials being present in their vermiculite interlayers in the clay fractions of these soils. Evidence for the latter occurrence is given by Mortland (1961) who reported that the presence of organic salts in the in-

terlayers of vermiculite could prevent or decrease the absorption of K. Also, Ross (1971) has reported that the removal of organic matter from mixed layer micaceous-vermiculite soil clays greatly increased K-fixation. Therefore, it seems quite likely that in the present study, the presence of interlayer organic molecules are blocking the entrance of potassium to wedge sites of micaceous vermiculite. Upon removal of these interlayer organic molecules, the K^+ is able to migrate to the wedge sites where it is selectively absorbed over Ca^{2+} . The Al-hydroxy polymers which are present probably serve to keep the vermiculite layers propped open and allow the K^+ ions to migrate to the wedge sites as suggested by Rich (1964). In addition, the Al-hydroxy polymers may be sterically blocking the entrance of the larger, hydrated calcium ions into the interlayer regions as suggested by Kozak and Huang (1971). Overall, these results suggest that organic matter interacting with layer silicates may have a significant influence in potassium selectivity and probably release of potassium from highly weathered soils of the humid tropics.

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Table 1. MINERAL CONTENT OF CLAY-SIZED FRACTIONS

	Catalina 0-15 cm Tropeptic Haplorthox Puerto Rico	Humatas 0-15 cm Typic Tropohumult Puerto Rico	Carimauga 8-20 cm Typic Haplustox Columbia
	----- % -----		
Mica	2	13	8
Vermiculite	4	11	4
Al-Chlorite	19	10	25
Kaolinite	44	38	29
Gibbsite	8	-	1
Amorphous	22	16	20

Fig. 1. X-ray diffractograms of the clay size fraction of the Carimagua soil following removal of interlayer Al-hydroxy polymers.

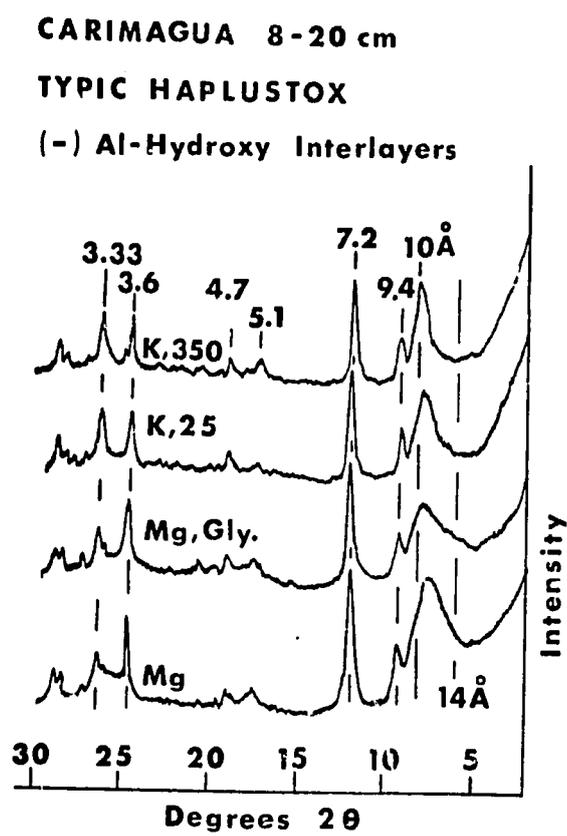


Fig. 2 CEC AND CES OF UNTREATED SURFACE HORIZONS

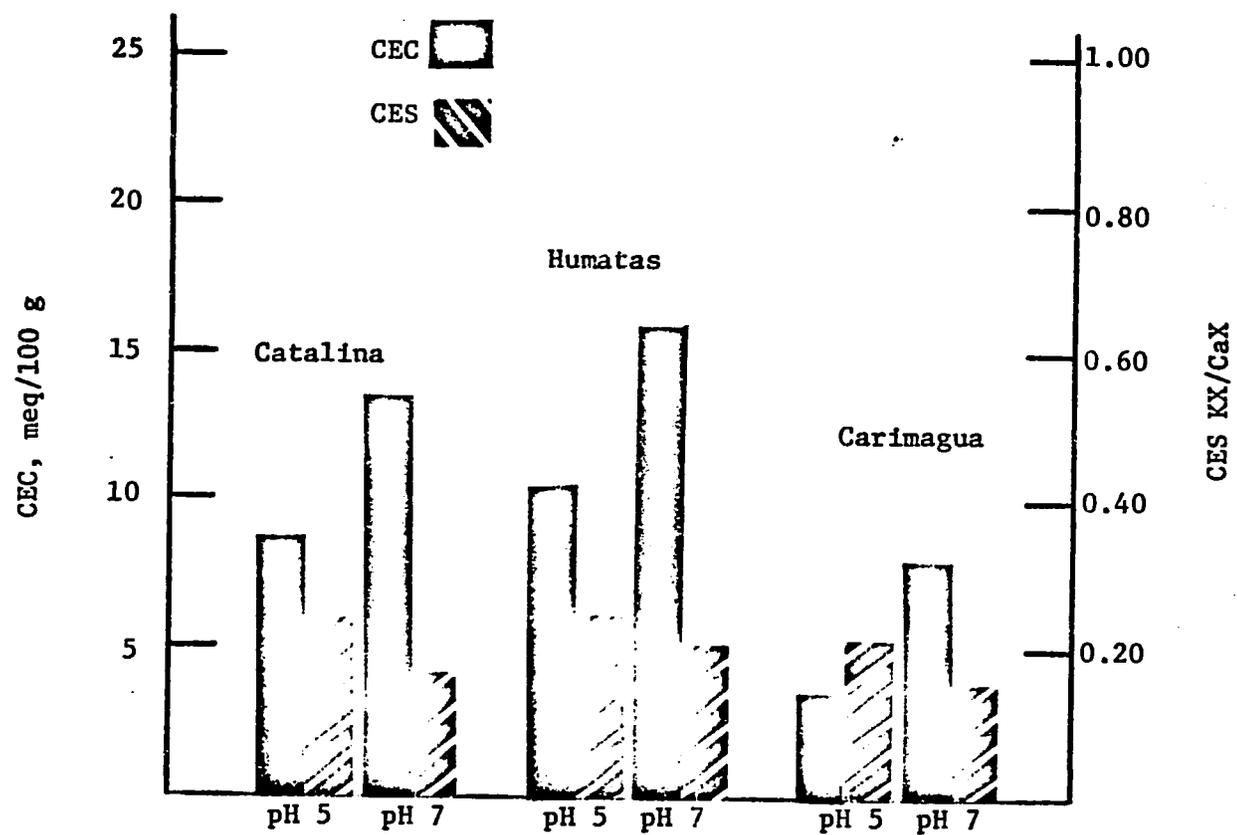


Fig. 3 CEC AND CES OF SURFACE HORIZONS TREATED FOR
REMOVAL OF ORGANIC MATTER

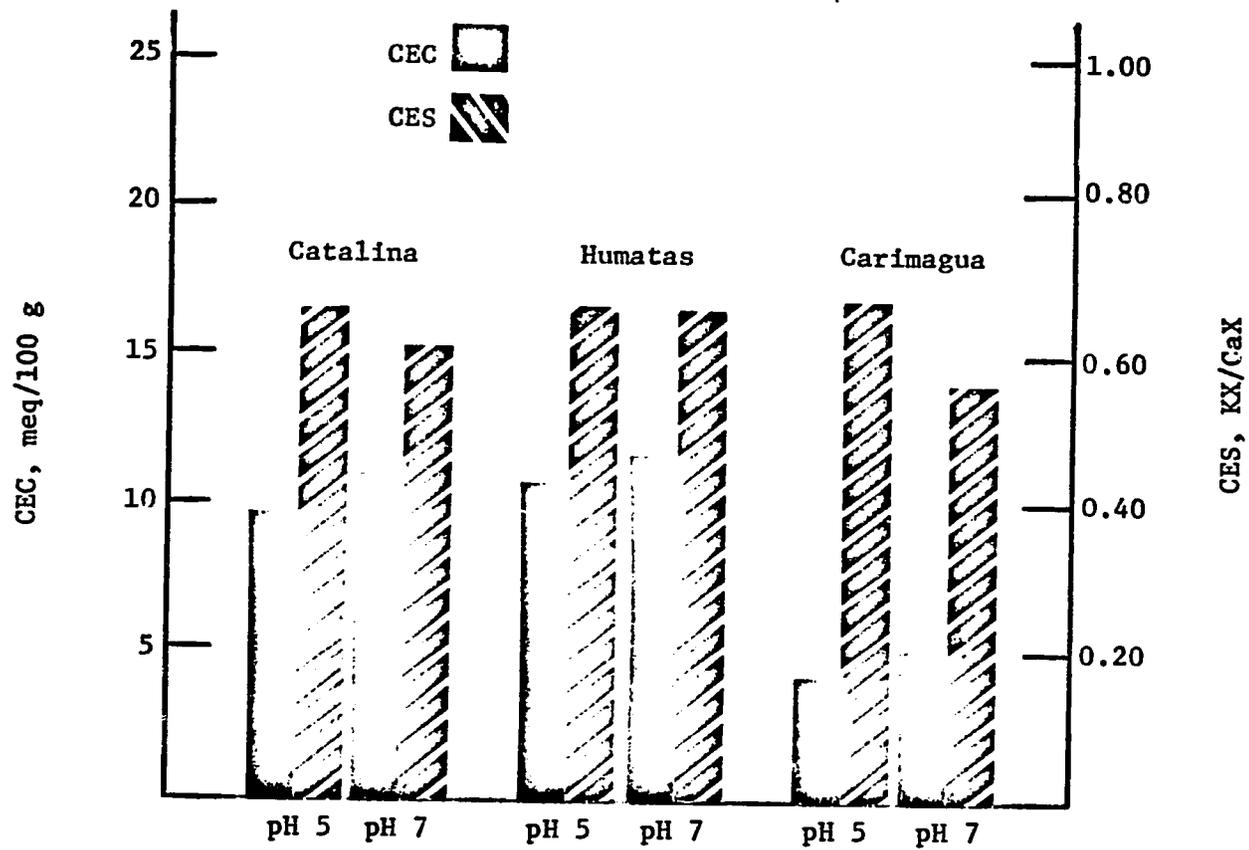


Fig. 4 CEC AND CES OF SURFACE HORIZONS TREATED FOR REMOVAL
OF AL-HYDROXY INTERLAYERS

