

SOIL MINERAL SURFACE PROPERTIES AS THEY RELATE  
TO THE IONIC AND SUSPENDED SOLUTES  
IN THE FLOWING SOIL SOLUTION

By

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## CHAPTER I

### INTRODUCTION

Soil mineral surface properties are of very great fundamental and practical importance in the study of the soil, in which nutrient elements required by plants are frequently held, and consequently their presence in the soil and their availability for plant growth depends on these properties. For example, the retention and availability of potassium added in fertilizers depend on the negatively charged surfaces in soils. Shrink-swell properties of soils are profoundly dependent, to a large extent, on the surface properties of soils. The high shrink-swell soils can sorb polar molecules on all layer surfaces. The accumulation of polar molecules in the clay interlayer spaces forces the layers apart, resulting in swelling of the clay and thus reducing the pore spaces in the soils. Therefore, drainage and the rate of movement of water and oxygen to plant roots are retarded.

The reaction of the soil clay mineral with organic compounds has been considered to be important. Organic compounds would be sorbed at clay mineral surfaces to form complexes of varying stabilities and properties. For example, some organic compounds derived from plant and animal remains and their decomposition products are strongly sorbed by clay minerals. In this interaction with the clay surface, some kinds of compounds may bridge between neighboring clay particles creating relatively stable aggregates, thus greatly influencing the moisture and



aeration properties of the soil. Other clay-organic interactions result in the protection of the organic compound from biological degradation. Biologically active compounds, such as herbicides and insecticides, may be sorbed by clay minerals and rendered inactive. When conditions have changed, these may be released to become reactive again or undergo catalytic degradation at the clay surface and completely lose their toxicity.

It has been reported that clay mineral surfaces of most Oklahoma soils contain hydroxy aluminum polymers (Allen and Reed, 1974). These polymers react in different manner with solutes in the soil solution, than they do with pure clay systems. Since certain forms of aluminum can be tightly held in the interlayer space of the clay mineral and are not easily exchangeable when placed in neutral salt solutions, thus they influence greatly the shrink-swell characteristics of Oklahoma soils, as well as the exchange characteristics.

It can be concluded from the above that the surface retention of clay minerals is the one single most important factor involved in understanding the fate of dissolved and suspended materials in the soil solution. The intensity of these surface reactions, when the soil solution passes through the soil, depends on total surface area, surface charge, charge density, organic matter, clay mineral composition, bulk density of the whole soil, percent free iron oxide, percent OH-Al interlayers, etc.

It is, therefore, necessary for more definitive research on the surface properties as they relate to the ionic and suspended solutes in the flowing soil solution. The research reported here will be an attempt to study those relationships.

## CHAPTER II

### LITERATURE REVIEW

A review of literature was carried out before the experimental work was begun. The review deals with:

1. Soil mineral surface properties, i.e., surface area, surface charge and distribution of charge source (tetrahedron vs. octahedral), and charge density.
2. Factors that affect the mineral surface properties of soils, i.e., organic matter, hydroxy-aluminum interlayer, and free iron oxide.
3. Soil mineral surface properties as they influence the ionic and suspended material in the flowing soil solution.

#### Soil Mineral Surface Properties

Soil mineral surface properties have long claimed the interest of agronomists. This is evidenced by the notable contributions which soil scientists, along with mineralogists, and other research workers, have made toward a better understanding of surface properties and the importance of these on physical and chemical properties of soil and on plant growth (Kelly, 1948; Marshall, 1949; and Fripiat, 1964).

Clays generally are composed of extremely small crystalline particles, thus they expose a large amount of external surface area. In some clays there are internal surfaces as well. This internal surface

occurs between the platelike crystal units that make up each particle. Thus, the tremendous surface area that characterizes clay is accounted for not only by small size but also by platelike structure of the small particle (Grim, 1968).

The determination of surface area is important since this property influences the physical and chemical properties, and it has also been used as a criterion for mineral identification. Determination of the specific surface of soil clays by ethylene glycol (Bower and Gschwend, 1952) or ethylene glycol monoethyl ether (Carter et al., 1965) is one of the major criteria being used to evaluate the surface properties of clays. Because of the importance of this, the ease with which its determination can be carried out and the simple equipment needed, it is widely reported in clay mineral studies.

The magnitude of the surface area value for a particular clay is influenced by the nature of the exchangeable ion on the clay. Thus Bower and Gschwend (1952) found that for Wyoming bentonite, as well as for a number of soils, the Ca- and H- saturated form have higher surface area values than Mg, Na,  $\text{NH}_4$  and K systems and in that order. The low values for  $\text{NH}_4$ - and K- saturated systems were understandable in view that the accompanying structure collapse would result in lowering of surface areas. The behavior of Mg and Na systems could not be explained from this point of view. McNeal (1963) found that the retention of ethylene glycol by montmorillonite, kaolinite, vermiculite, and illite were in the following order of cation saturation:  $\text{K} < \text{Na} < \text{Al} < \text{Ca}$ . He suggested that two additional glycol molecules are associated with Ca ions and that out of a value of 235-250 mg/g of ethylene retained by pure vermiculite and montmorillonite

samples, the cation-associated glycol can amount to 70-100 mg of glycol per g clay.

There are at least two ways to account for the negative charges associated with silicate clay particles. The first has been called "permanent" by Schofield (1949), implying that it is unchanged in magnitude or strength by changes in pH of the system. The permanent charge arises from the substitution of the silicon or aluminum atoms by an atom of similar geometry but of lower charge. This causes an excess negative charge to develop. It has been reported that the negative charge resulting from lattice substitutions are to be found mostly on cleavage surfaces, e.g., the basal cleavage surfaces of the layer clay minerals (Grim, 1968). Since the charges resulting from substitution in the octahedral sheet would act through a greater distance than the charges resulting from substitutions in the tetrahedral sheet, it would be expected that cations held because of the latter substitutions would be bonded by a stronger force than those held by forces resulting from substitutions in the octahedral sheet. In some cases, cations held by forces due to substitutions of aluminum for silicon seem to be substantially nonexchangeable, e.g., the potassium in the micas.

The second type of charge has been called by Schofield (1949) "pH-dependent". The reason for this pH-dependent charge is due to the dissociation of the H from SiOH groups, that is,  $\text{Si} - \text{OH} + \text{H}_2\text{O} = \text{SiO}^- + \text{H}_3\text{O}^+$ , on the clay surfaces as the pH of the clay is raised (Wiklander, 1964). Fripiat (1964) studied the character of the hydroxyls that develop at the broken edges of tetrahedral and octahedral units in relation to the cation exchange capacity. He found that the hydroxyls attached to the silicons are thermally more stable than those bound to

the aluminum.

Kelly (1948) has shown that in the 2:1 type minerals the permanent charge accounts for at least three-fourths of the cation exchange capacity whereas in kaolinite (1:1 type) the pH dependent charge is larger than that attributed to isomorphous substitution. Grim (1968) reported that cation exchange capacities of kaolinite and illite increase as the particle size decreases. In the case of expanding-lattice minerals, where most of the exchange is on accessible basal plane surfaces, it seems that particle size should make little difference. Johnson (1949) presented data showing a variation of cation exchange capacity with particle size for several montmorillonites and concluded that the difference in capacity was derived entirely from broken bonds. This conclusion, however, does not necessarily follow from Johnson's data, while Osthaus (1955) presented analytical data indicating no variation of cation exchange capacity with particle size for the smectites he studied.

Wiklander (1955) and others have reported that montmorillonite tends to hold  $\text{Ca}^{++}$  quite strongly compared to  $\text{K}^+$ , whereas the tendency is reversed in kaolinite. He reasoned that, since the C.E.C. of montmorillonite is about 10 to 20 times as great as that of kaolinite, the concentration of the exchange spots is higher. However, Bower (1959) has shown that the charge density of montmorillonite and kaolinite are about the same since the surface area of montmorillonite is so much larger than that of kaolinite. Denny and Roy (1964) suggested that, in general, bonding energies are greater for materials with greater charge density.

There are several methods for determining charge density but they

all give a biased mean value and do not yield information about the homogeneity of the isomorphous substitution (Stul and Mortier, 1974). The effect is due to chemical analysis and C.E.C. containing the broken bond. The C.E.C. further depends on the method of determination and varies to a large extent with the pH (Pratt, 1961).

## Factors that Affect the Mineral Surface Properties of Soils

### Organic Matter

The organic content of soil often is important in determining the properties of a clay material, and also a knowledge of clay-organic complexes might throw more light on physical, chemical, and biological properties of soils (Greenland, 1965a, 1965b). The sorption of organic materials by clays modifies the relationship of the clay to the surrounding environment in a fundamental way (Mortland, 1970). These modifications include interaction with water and salts as well as effects on swelling properties (Schnitzer, 1969). Inter- as well as intraparticle bonds results, and clay-organic complexes form into aggregates of varying size and stability which are of major importance in determining the physical nature of soil and, therefore, the environment it provides for plant growth (Greenland, 1965b).

The mechanism sorption of organic molecules by clay minerals is governed by the type of the charge possessed by the organic molecules. Ensminger and Giesecking (1941) considered that proteins can be sorbed on the exchange surfaces, and Van der Waals forces may be involved. Ruchrwein and Ward (1952) have shown that polycations but not polyanions

were sorbed in the interlamellar space of montmorillonite based on x-ray diffraction data. Greenland (1971) has shown that organic polycations and uncharged polymers are sorbed on the basal surfaces of clay minerals. On the other hand, it was shown that organic anions are normally repelled from the surfaces of negatively charged clay particles. Some sorption can occur on the position edge surfaces of clay particles and on hydroxy aluminum sites or through bridge linkages involving polyvalent cations (Schnitzer, 1969).

The importance of soil mineral surfaces and their reactions with organic compounds particularly pesticides has drawn considerable attention (Konrad et al., 1969; Yaron, 1975). Esfandiari (1970) has shown that clay minerals in Oklahoma soils sorb the herbicides paraquat and diquat. Weed and Weber (1969) found that the kind of exchangeable cation markedly affected sorption of diquat and paraquat by vermiculite but had much less effect on sorption by montmorillonite. Once sorbed, the two organic herbicides were much more difficult to exchange with salt solutions from montmorillonite than vermiculite. For most other organic pesticides which are weaker bases, their existence as cations and therefore their ability to exchange with metal ions on the clay will depend upon their ability to accept a proton from the surface acidity of clay minerals. Some s-triazines were shown to become protonated at clay mineral surfaces by Russell et al. (1968b). Weber (1966) demonstrated for a series of s-triazine compounds that the maximum sorption on montmorillonite occurred at a pH in the vicinity of the pKa value of each compound, that is, the pH at which the compound became protonated.

### Hydroxy-Aluminum Interlayer

It has been reported that certain forms of aluminum can be sorbed in interlayer spaces of vermiculite (Rich, 1960; Hsu and Bates, 1964). Hsu and Rich (1960) have shown that these aluminum forms are not easily replaced by cations common in soil and, therefore, reduce cation exchange capacity. Evidence from many sources (Rich, 1960; Shen and Rich, 1962; Jackson, 1963; Hsu and Bates, 1964) shows that aluminum occurs in interlayer positions in clays, often forming complete layers to which the term soil-chlorite is sometimes applied. The aluminum in such layers is not in the form of single hydrated aluminum ions but rather as polymeric ions that occur in solution. Lodging of the polymers in interlayer positions in montmorillonite and vermiculite minerals is promoted not only by their size and tendency to grow by addition of more aluminum laterally between the layers but also by the fact that the polymers are charged and are attached to exchange positions on both the layers. Jackson (1963) discussed at length the evidence for the marked stability of the polymers in interlayers in minerals, pointing out that aluminum released in soils during chemical weathering tends to accumulate in the form of interlayers in preference to the formation of gibbsite.

The aluminum in polymeric form in interlayers in silicate clays does not appear to be exchangeable to any significant degree. Barnhisel and Rich (1963) carried out a laboratory experiment in which polymeric aluminum was precipitated in interlayer positions in montmorillonite at different pH values and found that the exchange capacity was markedly reduced by the treatment. Interlayers produced where the molar ratio of hydroxyl to aluminum added was 0.35, 0.75, and 1.50 were stable



during the six months test period, and the clay did not gain in exchange capacity. Where the OH/Al ratio was 3 (corresponding to aluminum hydroxide and gibbsite), the C.E.C. was initially low; but the original exchange capacity was regained by the end of three months. The increase was associated with the formation of gibbsite. Hsu and Bates (1964) conducted a similar experiment with vermiculite and found that the aluminum interlayer did not form where the OH/Al ratio was 3 and gibbsite crystallized outside the clay particles within a few weeks. This evidence suggests that the blocking of exchange positions by polymeric interlayers is not necessarily permanent under the proper conditions.

#### Free Iron Oxide

A large portion of the total Fe in soils is frequently in the form of oxides. These oxides may exist as discrete particles, as coatings on soil mineral surfaces, and as a cement between mineral particles. Freshly formed iron hydroxides are known to be active in the sense that they have high isoelectric points and are therefore predominantly positively charged up to about pH 8 (Parks, 1965) and have very large surface areas (Mackenzie and Meldon, 1959). Iron oxide has also been shown to be associated with kaolin surfaces, at least at pH's below 5 (Follett, 1965) and may impart a predominantly positive charge to the iron-hydroxide-kaolinite complex (Summer, 1963). Greenland and Oades (1968) have described the conditions determining the association between iron hydroxides and kaolinite surfaces and they showed that iron hydroxide was precipitated onto the kaolinite surface only when precipitation occurred under acid conditions. The main factor determining whether the

iron hydroxide was attached to the clay surface or not was thought to be charge on the iron hydroxide, and precipitation at the isoelectric point leading to positively charged gel particles which were sorbed on the negatively charged basal surfaces of the kaolinite.

The quantitative determination of free iron oxides in soils is often of interest because of their effect not only on phosphate fixation but also on surface mineral properties. Several methods have been used to determine free iron oxide in soils (Dion, 1944; Jeffries, 1947; Aquilera and Jackson, 1953; Coffin, 1963). The most widely used methods employ sodium hydrosulphite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) as the reducing agent (Aquilera and Jackson, 1953) under a wide variety of conditions regarding buffers, pH, temperature, and reagent conditions.

Soil Mineral Surface Properties as They  
Influence the Ionic and Suspended  
Solute in the Flowing Soil  
Solution

When plants are grown in soil, many of the nutrient elements must move through the soil to reach the plant root surface before active metabolic processes may result in their uptake by the plant root. Barber (1962) has shown that three processes are involved in supplying nutrients to the plant root surface, they are: (1) root interception, (2) mass flow, and (3) diffusion. When ions are sorbed, the concentration of the ion in the soil solution is lowered, providing new ions are not immediately moved up to replace them, and a concentration gradient between root surface and surrounding soil is established. This concentration gradient can be replenished by the ions held by the soils. The

soil factors will also influence the rate at which the nutrient element reaches the plant root and, hence, its solubility.

The rate of reaction between the ions in the soil solution and the clay surface varies with the type of clay, and the kind and concentration of the ions. In general, the reaction for kaolinite is most rapid, being almost instantaneous. It is slower for montmorillonite and requires an even longer time for illites (Jarusov, 1937; Giesecking and Jenny, 1936). It has been found that the replacement of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$  by  $\text{Na}^+$  in Yolo clay loam soil of California increased as the concentration of  $\text{Na}^+$  in the solution increased (Kelly and Cummins, 1921). Wiklander (1955) showed that as the amount of exchangeable Ca on the clay mineral becomes less, the Ca becomes more and more difficult to release. Sodium, on the other hand, tends to become easier to release as the degree of saturation with sodium ions becomes less. Magnesium and potassium are not affected by the degree of saturation to the same extent as calcium and sodium. Kelly (1948) pointed out that the higher valence of the ion, the greater of its replacing power and the more difficult it is to displace when already present on the clay. Hydrogen is an exception since for the most part it behaves like a divalent or trivalent ion. It has been suggested that for ions of equal valence, those which are least hydrated have the greatest energy of replacement and are the most difficult to displace when already present on the clay (Page and Baver, 1939). Thus, lithium, although a very small ion, is considered to be highly hydrated and, therefore, to have a very large hydrated size.

From the review of literature, it is apparent that the surface reaction of clay minerals is one of the most important soil factors

influencing plant nutrient element availability. The soil mineral surface reacts with both organic and inorganic solutes in the soil solution and lends importance to the agronomic point of views. However, relatively little is known about soil mineral surface properties as they influence ionic and suspended solutes in the flowing soil solution. The study reported here is, therefore, an attempt to understand this relationship.

## CHAPTER III

### MATERIALS AND METHODS

#### Soil Studied

Soil samples were selected from three locations in the State of Oklahoma.

1. Bethany silt loam: Fine, Mixed, Thermic Pachic Paleustolls. Samples were taken from NW corner of SW1/4 of SE1/4 of section 15, T 19 N, R 2 E, Indian Meridian. The samples were collected from the following depths: 0-15, 15-30, 30-60, 60-90, and 90-120 cm.
2. Pond Creek silt loam: Fine-silty, Mixed-Thermic, Pachic Argiustolls. Samples were taken from the North Central Experiment Station at Lahoma, in Garfield County. The samples were collected from the following depths: 0-15, 15-30, 30-60, 60-90, and 90-120 cm.
3. Clairmont silt loam: Fine-silty, Mixed (Calcareous), Thermic, Typic Ustifluvents. Samples were taken approximately two miles east of the Foss Lake dam in Custer County, Oklahoma. This was in the NW1/4 NW1/4 NW1/4 of Section 6, T 12 N, R 19 W, Custer County. The samples were collected from the following depths: 0-15, 15-30, 30-45, 45-60, 60-75, 75-90, 90-105, 105-120, and 120-150 cm.

All the samples were air dried and passed through a 2 mm sieve.

#### Equilibrium Procedure

Fifty grams of each soil sample were weighed into a 50 ml leaching tube. A glass wool pad was placed in the bottom of each tube and a layer of fine quartz sand on top to reduce evaporation and disturbance of the surface due to addition of solutions. (Sand was acid washed to remove any ions present.)

Five sets of each soil sample were used with each set being saturated by a different extracting solution. Solutions used were distilled water, 1 N  $\text{NH}_4\text{Ac}$ , N HCl, N Acetic acid, N citric acid. Twenty milliliters of each solution were added to respective samples and allowed to equilibrate for 24 hrs. After equilibrium had been reached, the soil solution was removed under suction and analyzed for exchange cations ( $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ) using atomic adsorption (Perkin Elmer Atomic Adsorption 303).

#### Chemical Analyses

##### Hydroxy Aluminum Interlayer

Aluminum interlayer was extracted from a 5 gm soil sample with 50 ml portions of 1 N sodium citrate and heated in a water bath at 80-90°C as described by Frink (1965). The citrate solution was renewed four times every two hours with each extraction being preceded by cooling, centrifugation and decantation. The aluminum present in each extract was determined by the method of Jackson (1958).

### Free Iron Oxide

The samples were analyzed as described by Jackson (1958) with the modifications described by Lease (1968). Sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ) was used as the reducing agent.

### Organic Matter

Organic matter was determined by the modified Schollenberger procedure (Reed, 1974). Potassium dichromate and sulfuric acid were used. The sample was heated to  $165^\circ\text{C}$  and titrated with ferrous ammonium sulfate.

### pH Determination

A 1:1 ratio of soil and water was used to measure the pH as described by Peech (1965).

### C.E.C.

The method used to determine C.E.C. was described by Reed (1974). Ten grams of soil were shaken with 50 ml of 1 N  $\text{CaCl}_2$  for four hours or longer. The soil-salts mixture was filtered on a 55 cm Buchner funnel and leached three times more with 50 ml portions of 1 N  $\text{CaCl}_2$ . The sample was rinsed with de-ionized water, and leached three times with 50 ml of 1 N  $\text{NaNO}_3$ . The  $\text{NaNO}_3$  leachate was analyzed for Ca by E.D.T.A. titration and chloride in the  $\text{NaNO}_3$  solution was analyzed by Mohr titration.

### Surface Area

Surface area was determined by the ethylene glycol monoethyl ether (E.G.M.E.) method of Carter et al. (1965). Approximately 0.3 g of each sample, saturated with calcium, was placed in a weighing pan and dried in a vacuum desiccator over  $P_2O_5$  for 48 hours. The weighing pan and contents were then re-weighed and the weights of the dried sample recorded. Solvation with E.G.M.E. followed with 2 hours being allowed for equilibrium. The sample was then returned to the desiccator and dried in vacuum over  $CaCl_2$  to constant weight.

### Mechanical and Mineralogical Analyses

Mechanical analyses were determined by the hydrometer method (Day, 1956).

The silt and clay fractions were saved for x-ray diffraction analyses. The clay fraction was further separated into fine ( $< 0.2 \mu$ ) and coarse clay ( $2-0.2 \mu$ ) using the Sharples high speed steam turbine centrifuge (Jackson, 1973). X-ray diffraction patterns were obtained after addition of the clay suspension to porous ceramic slides and removal of excess moisture by vacuum. X-ray diffraction of clay samples was obtained on Ca saturated, ethylene glycol solvated, K saturated, and K saturated and heated to  $500^\circ C$  for four hours. All of the samples were x-rayed on a General Electric XRD 6 instrument with Ni-filtered  $Cu K_\alpha$  radiation generated at 30 KVP and 20 MA. Slits were  $1^\circ$  MR beam, HR sollar, and  $0.2^\circ$  detector.



## CHAPTER IV

### RESULTS AND DISCUSSION

#### Bethany Silt Loam

The results in Table V indicate that surface area and cation exchange capacity are related. When surface area is low, the cation exchange capacity is low. It appears that the surface area and cation exchange capacity, at the depth of 0-15 cm, are low, compared to the rest of the soil profile. The x-ray diffraction data show that montmorillonite, vermiculite, chlorite, illite, kaolinite, and quartz are present at all depths, in both the coarse and fine clay fractions. The silt fraction was also studied by x-ray diffraction and the results indicated that feldspars and quartz were the most pronounced minerals through all depths. The lowest readings of surface area and cation exchange capacity at the depth of 0-15 cm are not due to the type of clay minerals as illustrated by x-ray diffraction. However, the results of mechanical analyses as shown in Table II show that the amount of clays present at the depth of 0-15 cm is less than the lower depths. The difference in the amount of clays may probably cause the low readings of surface area and cation exchange capacity of the surface soils (0-15 cm).

From the results in Table I, it suggests that the highest extractable Al-compounds were from the top 0-15 cm. This probably indicates

that there has been more weathering in the top 0-15 cm depth than at the lower depths. According to many workers (Rich, 1960; Jackson, 1963; Hsu and Bates, 1964), the Al-compounds can be sorbed in interlayer spaces of montmorillonite and vermiculite, and reduce the cation exchange capacity of the minerals. The high extractable Al-compounds obtained in the top 0-15 cm from this study seems to support the low readings of cation exchange capacity and surface area in the top soils.

The pH reported in Table I ranges from 6.4 in the top layer to 7.8 in the bottom layer. In general, the pH tends to increase with depth. The organic matter content tends to decrease with depth, reaching a minimum at the depth of 90-120 cm. The high amount of free iron oxide appeared in the 60-90 cm and 90-120 cm depths.

The charge density obtained is based on surface area and cation exchange capacity. The results in Table IV showed that the charge density does not vary much through all depths. However, the charge density in the top 0-15 cm is higher than the other soils, although the results of surface area and cation exchange capacity are less than for the lower depths. From the results in Table V, it appears that the more soluble salts are present at the depth of 60-90 cm. The amounts of cations released seem to be higher at the depth of 60-90 cm when HCl, HOAc, and citric acid are used, but it is more or less the same release for  $\text{NH}_4\text{Ac}$  through all depths. Compared to the other ions, Na ions are easy to release. The highest amounts of cations were released with 1 N HCl and 1 N  $\text{NH}_4\text{Ac}$  extracting solutions, as compared to the release by 1 N HOAc and citric acid extracting solutions. The high amounts of cations released were not released at the highest charge density, nor highest surface area, nor highest cation exchange capacity of this soil.

A comparison of the data for the leaching and equilibrium procedures as shown in Table X indicates a difference in Ca/K ratio between the two procedures (i.e., equilibrium and leaching). The ratio of Ca/K in the equilibrium procedure is higher than the leaching procedure. Since it would appear that the equilibrium procedure is a better measure of field conditions, then it can be concluded that the plant roots are actually exposed to higher Ca/K ratio than is determined by leaching.

#### Pond Creek Silt Loam

The results in Table XI indicate that there is a good correlation between surface area and cation exchange capacity of this soil. Both surface area and cation exchange capacity are low in the top 0-15, 15-30 cm depths, compared to the lower depths. The mechanical analyses results in Table II show that the amounts of clay do not vary greatly through the profile. However, the x-ray diffraction data as shown in Table IV indicated that the types of clays are different between the upper and lower horizons. The clay fraction at 0-15 and 15-30 cm depth increments is composed primarily of illite, kaolinite, and quartz. On the other hand, montmorillonite which gave a 17-18° A reflection upon ethylene glycol solvation tends to be dominant at the depths of 30-60 and 60-90 cm. The high surface area and cation exchange capacity at the depth of 30 cm and below could, therefore, be due to the high montmorillonite content as indicated by x-ray diffraction results.

The results obtained for citrate extractable Al-interlayered from the three soils are shown in Table I. It appears that the interlayered Al-compounds of Pond Creek soil are higher in the top 30 cm than in the

TABLE I  
CHEMICAL PROPERTIES

Depth (cm)	C.E.C. me/100 g	Exchangeable Cations				pH 1:1 (soil:H <sub>2</sub> O)	Percent		
		Ca	Mg	K	Na		O.M.	Fe <sub>2</sub> O <sub>3</sub>	Al-Interlayer
<u>Pond Creek Silt Loam</u>									
0-15	9.2	5.3	2.0	1.3	0.1	5.9	1.6	0.6	2.8
15-30	15.5	9.6	3.8	1.0	0.1	6.7	1.5	0.4	2.4
30-60	23.6	14.3	7.3	1.1	0.2	7.3	1.1	0.5	1.8
60-90	23.6	18.8	6.6	0.9	0.4	7.7	0.8	0.6	1.4
90-120	17.2	12.5	5.3	0.7	0.6	7.7	0.5	0.6	1.6
<u>Bethany Silt Loam</u>									
0-15	11.3	7.5	1.5	0.3	0.3	6.4	1.5	0.6	2.3
15-30	19.8	12.3	3.1	0.3	1.0	6.6	1.3	0.8	1.4
30-60	25.0	12.8	3.5	0.3	1.7	7.3	1.2	0.5	1.1
60-90	19.2	14.8	2.8	0.3	2.0	7.8	0.7	1.0	1.0
90-120	18.2	10.3	2.8	0.3	2.0	7.8	0.5	1.3	1.5
<u>Clairmont Silt Loam</u>									
0-15	13.6	14.6	1.4	2.0	0.3	7.9	1.9	0.7	0.9
15-30	12.3	14.4	1.3	1.6	0.3	8.4	1.5	0.5	1.0
30-45	10.2	14.4	1.1	1.0	0.3	8.1	1.1	0.6	1.1
45-60	12.1	15.5	1.4	0.8	0.3	8.1	1.0	0.7	0.8
60-75	10.0	16.1	1.3	0.6	1.0	7.5	0.8	0.5	1.1
75-90	13.1	14.9	1.7	0.8	1.1	8.1	0.6	0.7	0.7
90-105	10.4	15.6	1.8	0.7	1.9	8.1	0.6	0.6	1.5
105-120	12.3	15.0	1.5	0.6	2.0	8.2	0.6	0.8	1.2
120-150	8.6	15.9	1.6	0.7	2.1	7.9	0.5	0.7	1.0

TABLE II  
MECHANICAL ANALYSES

Depth (cm)	% Clay	% Silt	% Sand
<u>Pond Creek</u>			
0-15	14	54	32
15-30	14	54	32
30-60	16	50	34
60-90	17	47	36
90-120	14	48	38
<u>Bethany</u>			
0-15	20	46	34
15-30	32	38	30
30-60	38	38	24
60-90	36	34	30
90-120	36	30	34
<u>Clairmont</u>			
0-15	16	48	36
15-30	14	50	36
30-45	12	48	40
45-60	14	50	36
60-75	12	48	40
75-90	14	50	36
90-105	12	54	34
105-120	14	54	32
120-150	10	50	40

TABLE III  
MINERALOGICAL DATA OF BETHANY SILT LOAM

Depth (cm)	Silt	Fine Clay	Coarse Clay
0-15	Q, F	M, V, C, I, K, Q	M, V, C, i, K, Q
15-30	Q, F	M, V, C, I, K, Q	M, V, C, I, K, Q
30-60	Q, F	M, v, c, i, Q	M, v, c, i, K, Q
60-90	Q, F	M, v, c, i, k, Q	M, v, c, i, K, Q
90-120	Q, F	m, v, c, K, Q	M, v, c, I, K, Q

M = montmorillonite

V = vermiculite

C = chlorite

K = kaolinite

I = illite

Q = quartz

F = feldspar

Capital letters = medium-strong peaks

Lower case letters = weak-medium peaks

TABLE IV  
MINERALOGICAL DATA

Depth (cm)	Silt	Fine Clay	Coarse Clay
<u>Pond Creek</u>			
0-15	Q, F	m, I, k, Q	I, K, Q
15-30	Q, F	i, k, Q	I, K, Q
30-60	Q, F	M, i, k, Q	M, i, k, Q
60-90	Q, F	M, I, k, Q	M, i, K, Q
90-120	Q, F	m, I, k, Q	m, I, K, Q
<u>Clairmont Silt Loam</u>			
0-15	Q, F	M, i, k, Q	M, i, K, Q
15-30	Q, F	M, i, Q	M, I, K, Q
30-45	Q, F	M, i, Q	M, I, k, Q
45-60	Q, F	M, i, Q	M, I, K, Q
60-75	Q, F	M, Q	M, I, K, Q
75-90	Q, F	M, i, Q	M, I, K, Q
90-105	Q, F	m, I, Q	M, I, K, Q
105-120	Q, F	M, i, Q	M, I, K, Q
120-150	Q, F	M, i, Q	M, I, K, Q

TABLE V

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY DISTILLED H<sub>2</sub>O;  
BETHANY SILT LOAM

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	50	11.3	6.5 x 10 <sup>4</sup>	.11	.04	.02	.3
15-30	104	19.8	5.5 x 10 <sup>4</sup>	.06	.03	.02	.5
30-60	129	25.0	5.6 x 10 <sup>4</sup>	.08	.04	.01	1.1
60-90	105	19.2	5.3 x 10 <sup>4</sup>	.20	.09	.02	1.9
90-120	100	18.2	5.3 x 10 <sup>4</sup>	.11	.04	.01	1.6

TABLE VI

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N NH<sub>4</sub>Ac;  
BETHANY SILT LOAM

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	50	11.3	6.5 x 10 <sup>4</sup>	19.2	9.3	.33	1.1
15-30	104	19.8	5.5 x 10 <sup>4</sup>	23.4	14.7	.07	2.6
30-60	129	25.0	5.6 x 10 <sup>4</sup>	20.2	14.0	.03	4.2
60-90	105	19.2	5.3 x 10 <sup>4</sup>	18.5	12.7	.09	5.0
90-120	100	18.2	5.3 x 10 <sup>4</sup>	19.2	12.7	.07	6.1



TABLE VII  
 RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
 TO CATIONS RELEASED BY 1 N HCl;  
 BETHANY SILT LOAM

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	50	11.3	6.5 x 10 <sup>4</sup>	36.4	15.7	.27	1.6
15-30	104	19.8	5.5 x 10 <sup>4</sup>	21.6	14.0	.04	2.7
30-60	129	25.0	5.6 x 10 <sup>4</sup>	22.4	16.7	.04	5.9
60-90	105	19.2	5.3 x 10 <sup>4</sup>	58.8	42.7	.07	17.4
90-120	100	18.2	5.3 x 10 <sup>4</sup>	22.6	14.5	.03	8.1

TABLE VIII  
 RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
 TO CATIONS RELEASED BY 1 N HOAc;  
 BETHANY SILT LOAM

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	50	11.3	6.5 x 10 <sup>4</sup>	9.5	6.2	.04	.1
15-30	104	19.8	5.5 x 10 <sup>4</sup>	9.5	6.2	.02	1.5
30-60	129	25.0	5.6 x 10 <sup>4</sup>	4.8	11.2	.02	3.0
60-90	105	19.2	5.3 x 10 <sup>4</sup>	35.0	28.8	.09	12.6
90-120	100	18.2	5.3 x 10 <sup>4</sup>	12.6	12.7	.03	4.7

TABLE IX

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N CITRIC ACID;  
BETHANY SILT LOAM

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	50	11.3	6.5 x 10 <sup>4</sup>	11.9	5.0	.06	.1
15-30	104	19.8	5.5 x 10 <sup>4</sup>	9.3	7.8	.04	2.5
30-60	129	25.0	5.6 x 10 <sup>4</sup>	15.2	9.0	.05	4.3
60-90	105	19.2	5.3 x 10 <sup>4</sup>	40.6	12.2	.06	6.6
90-120	100	18.2	5.3 x 10 <sup>4</sup>	6.4	8.3	.03	5.8

TABLE X

COMPARISON BETWEEN LEACHING AND EQUILIBRIUM OF  
Ca/K RATIO BASED ON me/100 g;  
BETHANY SILT LOAM

Depth cm	Leaching 1 N NH <sub>4</sub> Ac	Equilibrium			
		1 N NH <sub>4</sub> Ac	1 N HCl	1 N HOAc	1 N Citric â
0-15	25.9	58	135	238	198
15-30	42.2	334	540	475	233
30-60	37.5	673	560	240	304
60-90	43.3	205	840	389	677
90-120	30.1	274	753	420	213

lower horizons. These Al-compounds may be sorbed in the interlayer spaces of the 2:1 type minerals present in the soil, and are probably responsible for the low cation exchange capacity and surface area in the top layers. However, the x-ray diffraction results showed only small amounts of montmorillonite present in the fine clay (< 0.2  $\mu$  fraction) of the top 30 cm layers.

The silt fraction studied by x-ray diffraction shows that feldspars and quartz are present throughout all depths. Other major minerals in this soil were not found in this study.

Free iron oxide was determined and the results were shown in Table I. The data shows that the presence of free iron oxide is more or less the same throughout the profile. The difference in surface area and cation exchange capacity in the upper 30 cm depth and the lower horizons was not due to free iron oxide.

The results of the organic matter determination as shown in Table I indicated that the amount of organic matter decreases with depths. On the other hand, the pH reading increases with depths.

The results reported in Table XI shows that the charge density ranges from  $6.4 \times 10^4$  to  $8.3 \times 10^4$  esu/cm<sup>2</sup>. The highest reading was in the 15-30 cm sample, and the lowest value was in the 0-15 cm sample. It appears that the amounts of cations released are less at the 0-15 cm depth except when extracted with 1 N HCl. The low amounts of cations released probably relate to the low C.E.C., surface area, and charge density. However, the high charge density at the 15-30 cm depth apparently is not related to the amounts of cations released. The cations released seem to relate with the charge and surface area. The higher the charge and surface area, the greater the tendency for cations to

be released, which probably increases the availability of nutrient elements to plants.

The results reported in Table XI indicated that there are more soluble salts in the lower depths of the profile than in the surface layers. Sodium ions seem to be easily released from this soil as compared to Ca or Mg ions. The relative quantity of Na ions released are more or less the same with any extracting solution as shown in Tables XI through XV.

The results in Table XVI show that the ratio of Ca/K in both leaching and equilibrium procedure increases with depth. The ratio of Ca/K in the equilibrium procedure appears to be higher than that obtained by the leaching procedure. The equilibrium procedure is probably a better measure of field conditions since the soil samples are saturated with the extracting solution and are equilibrated for 24 hrs.

#### Clairmont Silt Loam

The results in Table XVII show that both surface area and cation exchange capacity do not vary much throughout this soil profile. The surface area ranges from 37 to 65 m<sup>2</sup>/g and the cation exchange capacity varies from 8.6 to 13.6 me/100 g. The mechanical analyses results as shown in Table II indicated that the percentage of sand, silt, and clay varies throughout the profile, but the actual quantities do not vary much through all depths. The mechanical analyses suggest that the soil is stratified. Alluvium is the parent material of this soil.

The x-ray diffraction data in Table IV show that the coarse clay fraction (2-0.2  $\mu$ ) is composed of montmorillonite, illite, kaolinite, and quartz throughout the profile. The studies of the fine clay

TABLE XI

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY DISTILLED H<sub>2</sub>O;  
POND CREEK

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	41.5	9.2	6.4 x 10 <sup>4</sup>	.11	.01	.09	.04
15-30	53.9	15.5	8.3 x 10 <sup>4</sup>	.20	.10	.04	.06
30-60	89.3	23.6	7.6 x 10 <sup>4</sup>	.21	.12	.03	.18
60-90	92.5	23.6	7.4 x 10 <sup>4</sup>	.60	.38	.04	.50
90-120	76.8	17.2	6.5 x 10 <sup>4</sup>	.38	.27	.03	.62

TABLE XII

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N NH<sub>4</sub>Ac;  
POND CREEK

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	41.5	9.2	6.4 x 10 <sup>4</sup>	2.0	1.7	.6	.1
15-30	53.9	15.5	8.3 x 10 <sup>4</sup>	2.9	2.2	.2	.1
30-60	89.3	23.6	7.6 x 10 <sup>4</sup>	2.9	2.5	.1	.2
60-90	92.5	23.6	7.4 x 10 <sup>4</sup>	2.3	2.4	.1	.4
90-120	76.8	17.2	6.5 x 10 <sup>4</sup>	2.3	2.5	.1	.6

TABLE XIII

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N HCl;  
POND CREEK

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	41.5	9.2	6.4 x 10 <sup>4</sup>	10.4	3.2	.53	.1
15-30	53.9	15.5	8.3 x 10 <sup>4</sup>	8.5	3.1	.10	.1
30-60	89.3	23.6	7.6 x 10 <sup>4</sup>	7.2	3.3	.04	.2
60-90	92.5	23.6	7.4 x 10 <sup>4</sup>	8.8	4.1	.04	.4
90-120	76.8	17.2	6.5 x 10 <sup>4</sup>	11.0	5.3	.05	.6

TABLE XIV

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N HOAc;  
POND CREEK

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	41.5	9.2	6.4 x 10 <sup>4</sup>	.8	.6	.10	.05
15-30	53.9	15.5	8.3 x 10 <sup>4</sup>	1.1	.9	.18	.05
30-60	89.3	23.6	7.6 x 10 <sup>4</sup>	1.3	1.1	.12	.23
60-90	92.5	23.6	7.4 x 10 <sup>4</sup>	2.3	2.1	.08	.31
90-120	76.8	17.2	6.5 x 10 <sup>4</sup>	1.9	1.6	.06	.42

TABLE XV

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N CITRIC ACID,  
POND CREEK

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	41.5	9.2	6.4 x 10 <sup>4</sup>	2.0	.1	.19	.05
15-30	53.9	15.5	8.3 x 10 <sup>4</sup>	3.8	1.0	.06	.05
30-60	89.3	23.6	7.6 x 10 <sup>4</sup>	3.4	1.0	.06	.24
60-90	92.5	23.6	7.4 x 10 <sup>4</sup>	3.5	1.1	.07	.33
90-120	76.8	17.2	6.5 x 10 <sup>4</sup>	3.6	1.2	.13	.42

TABLE XVI

COMPARISON BETWEEN LEACHING AND EQUILIBRIUM OF  
Ca/K RATIO BASED ON me/100 g;  
POND CREEK

Depth cm	Leaching 1 N NH <sub>4</sub> Ac	Equilibrium			
		1 N NH <sub>4</sub> Ac	a N HCl	1 N HOAc	1 N Citric $\hat{a}$
0-15	4.1	3.2	19.5	8.4	10.5
15-30	9.2	16.8	85.0	6.3	63.3
30-60	13.6	40.7	180.0	11.0	57.3
60-90	21.8	37.5	219.0	29.3	50.0
90-120	18.4	37.5	220.0	31.2	27.4

fraction indicated that montmorillonite and illite are the dominant clay minerals through all depths. Kaolinite was not detectable in the fine clay fraction. The quartz content tends to be relatively uniform through all depths. The silt fraction is composed largely of feldspars and quartz. Montmorillonite, illite, and kaolinite were not found in the silt fraction studied.

From the mineralogical analyses results, it suggests that the difference in surface area and cation exchange capacity in the profile is not due to the types of clays, but mainly due to the amounts of clays.

The chemical analyses results as shown in Table I indicate that pH of this soil is high throughout the profile, ranging from 7.5 to 8.4. The exchangeable cations are higher than the cation exchange capacity. This suggests that this soil contains free calcium carbonate. The free calcium carbonate was observed when the soil was extracted with acid.

The results in Table I show that the organic matter content is higher in the top soil and decreases with depth. The percentage of free iron oxide is more or less the same throughout the profile and ranges from 0.46% to 0.76%. The data obtained from sodium citrate extractable Al-compounds show that the amounts of Al-interlayer in the clay remained essentially constant through all depths.

The results as shown in Tables XVII through XXI indicated that the charge density varied from  $6.4 \times 10^4$  to  $9.7 \times 10^4$  esu/cm<sup>2</sup>, and the higher charge density appears at the lower depths (below 60 cm). The amounts of cations released by different extracting solutions do not vary much through all depths. The results seem to indicate that the charge density and the amounts of cations released are not related. The



charge density at the depth of 0 to 15 cm was  $8.4 \times 10^4$  esu/cm<sup>2</sup> which was higher than the charge density at the 15 to 60 cm depth and lower than the charge density at the 60 cm depth, but the amounts of cations released are more or less the same through all depths. The cations released are those that are available to plants. Therefore, it can probably be said from the results that the availability of plant nutrient elements does not relate to the charge density when different extracting solutions are passed by the soil mineral surfaces. However, the amounts of cations released by each extracting solution as well as the charge and surface area do not vary much through all depths.

It was reported in Table XX that the amounts of calcium ions released by 1 N HOAc are higher, compared to the amounts of calcium ions released by other extracting solutions. This is probably due to the free colloidal calcium carbonate in this soil. The free calcium carbonate also caused the lesser amounts of cations to be released by 0.1 N HCl, because the 0.1 N HCl solution reacted with calcium carbonate and very few of the cations at the exchange sites were replaced by hydrogen ions. If a higher concentration of HCl is used, more cations would probably be released from the soil.

The results in Table XXII show that the ratio of Ca/K increases with depth for both the leaching and equilibrium procedures, with the exception of 1 N NH<sub>4</sub>Ac. In this case the ratio increases up to 105 cm and then decreases. When the same extracting solution (1 N NH<sub>4</sub>Ac) is used for both procedures, the leaching procedure showed a higher Ca/K ratio. When the equilibrium procedure was run with three other extracting solutions (.1 N HCl, 1 N HOAc, and 1 N citric acid) the results

showed a higher Ca/K ratio than in the leaching procedure. This may be due to the reaction of the acid with free calcium carbonate in the soil.

TABLE XVII

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY DISTILLED H<sub>2</sub>O;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	.4	.1	.24	.03
15-30	61	12.3	7.0 x 10 <sup>4</sup>	.4	.1	.24	.03
30-45	54	10.2	6.7 x 10 <sup>4</sup>	.4	.1	.12	.03
45-60	65	12.1	6.4 x 10 <sup>4</sup>	.4	.1	.07	.03
60-75	40	10.0	9.6 x 10 <sup>4</sup>	.4	.1	.06	.05
75-90	52	13.1	9.0 x 10 <sup>4</sup>	.4	.1	.04	.05
90-105	41	10.4	9.7 x 10 <sup>4</sup>	.5	.2	.05	.08
105-120	49	12.3	9.1 x 10 <sup>4</sup>	.5	.2	.05	.10
120-150	37	88.6	9.2 x 10 <sup>4</sup>	.5	.2	.04	.10

TABLE XVIII

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N NH<sub>4</sub>Ac;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	6.0	1.3	3.0	.3
15-30	61	12.3	7.0 x 10 <sup>4</sup>	4.9	1.0	1.6	.3
30-45	54	10.2	6.7 x 10 <sup>4</sup>	6.2	1.2	1.5	.3
45-60	65	12.1	6.4 x 10 <sup>4</sup>	5.8	1.2	.8	.3
60-75	40	10.0	9.6 x 10 <sup>4</sup>	6.1	1.3	.5	.9
75-90	52	13.1	9.0 x 10 <sup>4</sup>	5.7	1.4	.5	1.0
90-105	41	10.4	9.7 x 10 <sup>4</sup>	6.1	1.6	.5	1.8
105-120	49	10.4	9.1 x 10 <sup>4</sup>	5.4	1.5	.6	2.0
120-150	37	8.6	9.2 x 10 <sup>4</sup>	6.4	1.8	.7	2.1

TABLE XIX

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY .1 N HCl;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	3.3	.7	.8	.2
15-30	61	12.3	7.0 x 10 <sup>4</sup>	3.8	.8	.7	.2
30-45	54	10.2	6.7 x 10 <sup>4</sup>	3.5	.7	.5	.2
45-60	65	12.1	6.4 x 10 <sup>4</sup>	3.7	.8	.3	.2
60-75	40	10.0	9.6 x 10 <sup>4</sup>	3.7	.9	.2	.5
75-90	52	13.1	9.0 x 10 <sup>4</sup>	3.5	.8	.1	.6
90-105	41	10.4	9.7 x 10 <sup>4</sup>	3.5	.9	.1	.7
105-120	49	12.3	9.1 x 10 <sup>4</sup>	6.3	1.9	.2	.9
120-150	37	8.6	9.2 x 10 <sup>4</sup>	6.9	1.1	.2	1.0

TABLE XX

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N HOAc;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	21.1	5.1	1.9	.3
15-30	61	12.3	7.0 x 10 <sup>4</sup>	20.2	4.0	1.2	.3
30-45	54	10.2	6.7 x 10 <sup>4</sup>	21.1	3.2	.9	.3
45-60	65	12.1	6.4 x 10 <sup>4</sup>	21.1	4.1	.5	.3
60-75	40	10.0	9.6 x 10 <sup>4</sup>	32.1	8.3	.5	.9
75-90	52	13.1	9.0 x 10 <sup>4</sup>	20.5	3.5	.3	1.0
90-105	41	10.4	9.7 x 10 <sup>4</sup>	20.5	4.3	.3	1.6
105-120	49	12.3	9.1 x 10 <sup>4</sup>	20.5	5.4	.3	2.0
120-150	37	8.6	9.2 x 10 <sup>4</sup>	19.5	4.8	.3	2.0

TABLE XXI

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 1 N CITRIC ACID;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	5.9	1.2	.8	.1
15-30	61	12.3	7.0 x 10 <sup>4</sup>	3.6	.6	.3	.1
30-45	54	10.2	6.7 x 10 <sup>4</sup>	3.6	.7	.3	.1
45-60	65	12.1	6.4 x 10 <sup>4</sup>	3.4	.5	.1	.1
60-75	40	10.0	9.6 x 10 <sup>4</sup>	4.1	.9	.2	.2
75-90	52	13.1	9.0 x 10 <sup>4</sup>	2.9	.8	.1	.3
90-105	41	10.4	9.7 x 10 <sup>4</sup>	4.1	1.2	.1	.4
105-120	49	12.3	9.1 x 10 <sup>4</sup>	2.9	.9	.1	.6
120-150	37	8.6	9.2 x 10 <sup>4</sup>	3.7	1.3	.1	.6

TABLE XXII

COMPARISON BETWEEN LEACHING AND EQUILIBRIUM OF  
Ca/K RATIO BASED ON me/100 g;  
CLAIRMONT

Depth cm	Leaching 1 N NH <sub>4</sub> Ac	Equilibrium			
		1 N NH <sub>4</sub> Ac	1 N HCl	1 N HOAc	1 N Citric a
0-15	7.3	3.0	4.1	11.3	7.5
15-30	9.0	3.0	5.2	16.3	10.6
30-45	14.4	4.2	7.7	24.5	13.8
45-60	19.4	7.0	13.5	42.0	28.5
60-75	26.8	12.2	21.5	64.0	21.5
75-90	18.6	11.4	24.6	82.0	57.4
90-105	22.3	12.1	24.6	82.0	40.6
105-120	25.0	9.2	30.0	82.0	57.4
120-150	22.7	9.6	40.6	78.0	52.9

## CHAPTER V

### SUMMARY AND CONCLUSIONS

The results reported in this study show no relationship between charge density and the amount of cations released, but the data suggest that the soils of high charge density and high surface area tend to provide more nutrient elements to the soil solution for plant nutrition. The sodium ions appear to be easily released, compared to calcium or magnesium ions.

The investigations of hydroxy-aluminum interlayer show that the top soils of Bethany and Pond Creek contain more hydroxy-aluminum compounds than the subsoils. This suggests that more weathering has occurred in the top soils than in the soil at lower depths.

In these experiments, it has been assumed that cations on the exchange surfaces are not released by distilled water, and the amount of organic matter is too small to affect the surface charge of the whole soil. The presence of free  $\text{CaCO}_3$  and salts might interfere with the interpretation of these results because when the soil samples were saturated with HCl, HOAc, or citric acid, the acids would be neutralized by  $\text{CaCO}_3$  and only small amounts of H ions would be available for replacing the cations on the exchange mineral surfaces. This may complicate the interpretation of these results with respect to the relationships of soil mineral surfaces to ions or suspended solutes in the flowing soil solution.

The charge density obtained was based on surface area and C.E.C. The soils of high surface and C.E.C. may have the same charge density as the soils of low surface area and C.E.C. The soils of high C.E.C. adsorb more exchangeable cations and have a tendency to release more cations. However, the data obtained here were not tested by statistical analyses because only one replication of each soil was taken from each location. It would probably take at least four or five replications from each location to obtain results that statistical analyses could be used for obtaining results that would be more reliable.

If this research is expanded, fine textured mature soils of widely different character should be selected because additional research is dealing with clay minerals and mature acid soils should provide comparison between horizons in the profile.

Varying concentrations of extracting solutions should be used so that the results can be compared on a more quantitative basis when the soil sample is equilibrated with dilute and concentrated extracting solutions.

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TABLE XXIII

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 0.001 N HCl;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	0.5	.17	.45	.23
15-30	61	12.3	7.0 x 10 <sup>4</sup>	0.3	.10	.27	.24
30-45	54	10.2	6.7 x 10 <sup>4</sup>	0.2	.07	.15	.24
45-60	65	12.1	6.4 x 10 <sup>4</sup>	0.2	.07	.09	.24
60-75	40	10.0	9.6 x 10 <sup>4</sup>	0.2	.05	.06	.53
75-90	52	13.1	9.0 x 10 <sup>4</sup>	0.2	.08	.06	.62
90-105	41	10.4	9.7 x 10 <sup>4</sup>	0.8	.19	.08	.71
105-120	49	12.3	9.1 x 10 <sup>4</sup>	0.7	.21	.07	1.01
120-150	37	8.6	9.2 x 10 <sup>4</sup>	0.8	.21	.07	1.61

TABLE XXIV

RELATIONSHIPS OF SURFACE AREA, C.E.C., CHARGE DENSITY  
TO CATIONS RELEASED BY 0.00001 N HCl;  
CLAIRMONT

Depth cm	Surface Area m <sup>2</sup> /g	C.E.C. me/100 g	Charge Density esu/cm <sup>2</sup>	me/100 g			
				Ca	Mg	K	Na
0-15	57	13.6	8.4 x 10 <sup>4</sup>	0.3	.06	.22	.21
15-30	61	12.3	7.0 x 10 <sup>4</sup>	0.1	.04	.13	.23
30-45	54	10.2	6.7 x 10 <sup>4</sup>	0.1	.04	.09	.23
45-60	65	12.1	6.4 x 10 <sup>4</sup>	0.1	.04	.05	.23
60-75	40	10.0	9.6 x 10 <sup>4</sup>	0.2	.04	.03	.51
75-90	52	13.1	9.0 x 10 <sup>4</sup>	0.2	.06	.03	.55
90-105	41	10.4	9.7 x 10 <sup>4</sup>	0.2	.06	.04	.60
105-120	49	12.3	9.1 x 10 <sup>4</sup>	0.4	.11	.03	.91
120-150	37	8.6	9.2 x 10 <sup>4</sup>	0.2	.06	.03	.94

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