

ELECTROKINETIC BEHAVIOR OF A PALEUDULT PROFILE IN RELATION TO MINERALOGICAL COMPOSITION

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ABSTRACT

By means of electrokinetic measurements, we investigated the pH-dependent surface charge characteristics of soils from eight horizons of a Dothan soil profile from the Atlantic Coastal Plain. The zero point of charge (ZPC) varied from a low value (~ 2) in the Ap horizon, increased abruptly with the transition from the A2 to the B1t horizon, and attained a value in the range of 7 to 8 in the B2 horizons. This increase in ZPC with depth is primarily a manifestation of a corresponding elevation in iron content with depth, inasmuch as iron removal from the B25tpl horizon reduced the ZPC from 7.9 to 2.3. The ability of 1 to 3 percent Fe to impart to the soil electrokinetic properties characteristic of pure hydrous iron oxides supports the belief that iron occurs principally as coatings, rather than discrete mineral entities, in the soil matrix. Specific adsorption of Ca^{2+} at the soil-solution interface made it difficult to establish a unique, well-defined ZPC for some of the soils. The findings suggest that, at typical field pH, the B2 horizon soils have a pH-dependent anion exchange capacity that will influence movement of certain plant nutrients through the soil and may mitigate the extent of NO_3^- leaching to groundwater from land application of wastewaters, sludges, and nitrogenous agricultural residues.

INTRODUCTION

Soil surface charge characteristics play a decisive role in determining several properties of major agricultural importance. Interfacial reactions with solution components often occur in response to an electrostatic driving force, i.e., ionically charged solutes sorbing on oppositely charged surfaces (Elliott and Huang 1979). The ion-binding properties of soils are, therefore, of fundamental significance in controlling the plant availability of applied nutrients and the fate of pollutants in the soil system. Additionally, soil structural and charge characteristics are inextricably related, for the magnitude and sign of the soil charge govern dispersion/flocculation properties of the soil matrix (El-Swaify 1976). Maintaining soil particles in a flocculated state is essential for adequate water infiltration, gas transfer, and reduced susceptibility to erosional losses. Understandably enough, soil surface charge properties have received considerable attention in the recent soil chemistry literature

(Laverdiere and Weaver 1977; Hendershot et al. 1979; Parker et al. 1979).

A convenient descriptor for assessing the sign and magnitude of the surface charge of soils is the zero point of charge (ZPC). The ZPC is the pH value at which the surface charge, arising from interaction of the surface with all solution components (i.e., H^+ , OH^- , background electrolyte ions, solid dissolution products), is zero (Parks 1967). At pH values more acidic than the ZPC, the soil particles carry a net positive charge, while conditions more alkaline than the ZPC result in electronegative soil colloids. Most colloids in nature, including many soil particles, have ZPCs in the acidic pH range and, thus, are net negatively charged at near neutral pH.

Operationally, ZPC can be determined by a variety of direct techniques, such as potentiometric titrations, ion adsorption studies, and electrokinetic measurements, and it can be inferred from coagulation kinetics studies, maximum sedimentation rates, and heat of immer-

sion values (Stumm and Morgan 1970). Titration experiments appear to be the most popular soil ZPC assessment technique (Hendershot 1978; Hendershot et al. 1979), and soil surface charge characterization using electrokinetic measurements appears less frequently (Huang et al. 1977). Electrophoresis, the electrokinetic technique of greatest practical relevance, is based on the principle that charged colloidal particles suspended in a solvent will migrate in response to an applied potential gradient. The velocity and direction of the resulting motion depend on the magnitude and sign, respectively, of the colloid surface charge. For more detail on the theory and measurement of electrokinetic effects and their use in documenting ZPCs, see the work of Shaw (1970), Sennett and Oliver (1965), and Parks (1965).

Although pure crystalline oxides, hydroxides, carbonates, and the like generally have unique, well-defined ZPC values, soils can exhibit a wide range of ZPC values because of their heterogeneity. Proceeding from simple oxide systems to soils, one can predict, at least semiquantitatively, ZPC values on the basis of mineralogical composition (Parks 1967). For example, it has been observed that aluminosilicates have ZPC values intermediate between that of pure silica (ZPC ~2) and alumina (ZPC ~9), depending on their Si/Al ratio (Smolik et al. 1966). Parks (1967) suggests that the ZPC of any complex oxide is roughly the weighted average of the component isoelectric points. It seems quite nat-

ural to extend this concept to soils to include all organic, as well as inorganic, surfaces (Hendershot et al. 1979).

This study examined charge characteristics of eight horizons of a Dothan (Plinthic Paleudults) profile from the Atlantic Coastal Plain. Crop production on these soils is of major importance to the local economy, and waste disposal on these soils will undoubtedly accelerate in the future, for large population centers exist within the region. Despite this, data on the charge characteristics of such soils are meager (Huang et al. 1977). This study was initiated to investigate the pH-dependent charge characteristics and document the ZPC for these soils, using electrophoresis. The results have been interpreted against the mineralogical variations in the soil profile. Implications of the data to the interaction of ionic solutes in the soil-water environment are explored.

MATERIALS AND METHODS

Soil collection and treatment

Studies were conducted on eight horizons from a Dothan soil (fine-loamy, siliceous, thermic Plinthic Paleudults) profile located in the Atlantic Coastal Plain. Bulk samples were taken from the Ap, A2, B1t, B21t, B22t, B23tpl, B24tpl, and B25tpl horizons.

Chemical, mineralogical, and physical properties were determined as described previously (Sparks et al. 1980a); see Table 1.

TABLE 1
Selected chemical, mineralogical, and physical properties of Dothan soil

Horizon	Depth, cm	Particle size analysis			pH	Exchangeable bases				Mineral suite of <2 μ m clay fraction ^a
		Sand	Silt %	Clay		Ca	Mg meq/100 g	Na	K	
Ap	0-15	70.07	20.92	9.01	5.7	1.73	0.85	0.01	0.13	VC ₁ ^b KK ₂ QZ ₃ GI ₄
A2	15-33	63.20	24.20	12.60	4.9	0.31	0.11	0.02	0.43	VC ₁ VR ₂ KK ₃ MI ₄ QZ ₅
B1t	30-41 ^d	55.87	24.27	19.86	4.7	0.46	0.17	0.03	0.11	VC ₁ KK ₂ GI ₃ QZ ₄
B21t	41-76 ^d	44.03	21.76	34.21	4.9	0.78	0.38	0.02	0.16	VC ₁ KK ₂ GI ₃ QZ ₄
B22t	76-104 ^d	36.39	10.81	52.80	4.7	0.11	0.56	0.04	0.13	KK ₁ VC ₂ GI ₃ QZ ₄
B23tpl ^c	104-124 ^d	42.81	10.91	46.28	4.9	0.06	0.33	0.03	0.10	KK ₁ VC ₂ VR ₃ GI ₄ QZ ₅
B24tpl	124-168 ^d	48.73	10.05	41.22	4.7	0.03	0.17	0.02	0.07	KK ₁ VC ₂ GI ₃ QZ ₄
B25tpl	137-165	49.75	9.20	41.05	4.7	0.03	0.20	0.02	0.05	KK ₁ VC ₂ QZ ₃ GI ₄

^a VC = chloritized vermiculite; VR = vermiculite; MI = mica; KK = kaolinite; QZ = quartz; GI = gibbsite.

^b Subscript 1 = most abundant; 5 = least abundant.

^c Denotes 10 to 15% plinthite nodules, which are Fe-rich, humus-poor mixtures of clay with quartz.

^d These samples were taken using an auger from the same sampling area.

Iron oxides from the B25tpl horizon were removed by three 24-h room temperature extractions, using the sodium-citrate-bicarbonate-dithionite method of Mehra and Jackson (1960).

Electrokinetic measurements

The electrokinetic properties of the suspended soil colloids were measured using a Zeta-meter (Zeta Meter, Inc.). It consists of a variable (0 to 300 V) DC power supply, an American Optical stereoscopic microscope (Model 26L), and a Riddick electrophoresis cell with a molybdenum anode and platinum-iridium cathode. The Zeta-meter allows viewing of dilute (10 to 2000 ppm) colloidal suspensions at 60, 90, and 120 X magnification. A detailed treatment on the use of the Zeta-meter for studying colloidal systems is given by Riddick (1968).

Soil suspensions were first prepared by adding 0.5 g of soil to 250 ml of a 0.01 M CaCl₂ solution prepared from distilled water. While the suspensions were being stirred, the pHs were measured with an Orion 901 pH meter equipped with a combination electrode, and pH adjustment was made using standard acid (HCl or HClO₄) and base (NaOH). The suspension was introduced into the electrophoresis cell, and a voltage (50 to 100 V) was applied. The migration of the soil particles from one side of the field to the other (the direction depending on their net charge) was viewed microscopically. The time to traverse a known distance (generally 40 to 80 μ m) was measured for each particle. Normally, 10 particles for each sample at a predetermined pH were tracked, and the average velocity was recorded. The electrophoretic mobility (EM), or velocity per applied potential gradient, was calculated by

$$EM = \frac{\text{velocity}}{\text{potential gradient}} = \frac{x/t}{v/10} = \frac{10x}{vt}$$

where EM has units of micrometers/second/volt/centimeter, x is the tracking distance (μ m), v is the applied voltage (V), t is the average time in seconds to travel a distance x , and the number 10 is the distance in centimeters between electrodes. The sample temperature was also recorded, and all EM values reported have been adjusted to 25°C, using the chart provided in the Zeta-meter operating manual, which corrects for the temperature-dependence of the viscosity and dielectric constant of the suspending aqueous solution.

RESULTS AND DISCUSSION

Soil mineralogy and ZPC

The electrokinetic characteristics of the soil horizons as a function of solution pH are shown in Fig. 1. The electrophoretic mobility (EM) values ranged from -1 to $+2$ μ m/sec/V/cm, which were, in general, smaller than EM values found for pure oxides and other mineralogically different soils (Huang et al. 1977).

The Ap and A2 horizons were electronegative over the entire pH range of investigation, and they exhibited very low ZPC values of about 2 (Fig. 1). A negative surface at neutral pH is characteristic of most suspended solids encountered in nature, including many insoluble oxides (Stumm and Morgan 1970). Furthermore, the ZPCs of many soils are reported to be in the pH 2 to 5 range (Morais et al. 1976; Huang et al. 1977; Laverdiere and Weaver 1977; Hendershot and Lavkulich 1979).

The precise reason for such low ZPC values must be related to the soil compositional characteristics. From observed ZPC values for soils that differ substantially only in their organic matter content, a number of investigators (van Raij and Peech 1972; Morais et al. 1976) suggest that organic matter lowers ZPC. Hendershot and Lavkulich (1979) provide experimental evidence confirming that hypothesis. Organic matter owes its charge to the presence of dissociable functional groups, although the proton dissociation constants of the common functional groups are generally greater than 4.0 (Tanford 1961), which cannot account for such low ZPC values. However, for complex multifunctional macromolecules like soil organic matter, interaction between neighboring sites can alter the observed dissociation constants (Tanford 1961). This is consistent with the data presented by Balajee and Iwasaki (1969), which indicated that starches are negatively charged over the pH 3 to 11 range and appear to have ZPCs below 2.0.

Though it is clear that the presence of organic matter can materially affect soil ZPC, it was relatively unimportant in this study. Although the ZPCs in the Dothan profile vary over a wide range, the organic matter content is relatively constant, the Ap horizon excepted (Table 2). Furthermore, the Ap and A2 soils have identical ZPC values, despite a substantially different organic matter content. The low ZPCs of the A horizons are more likely reflective of an abun-

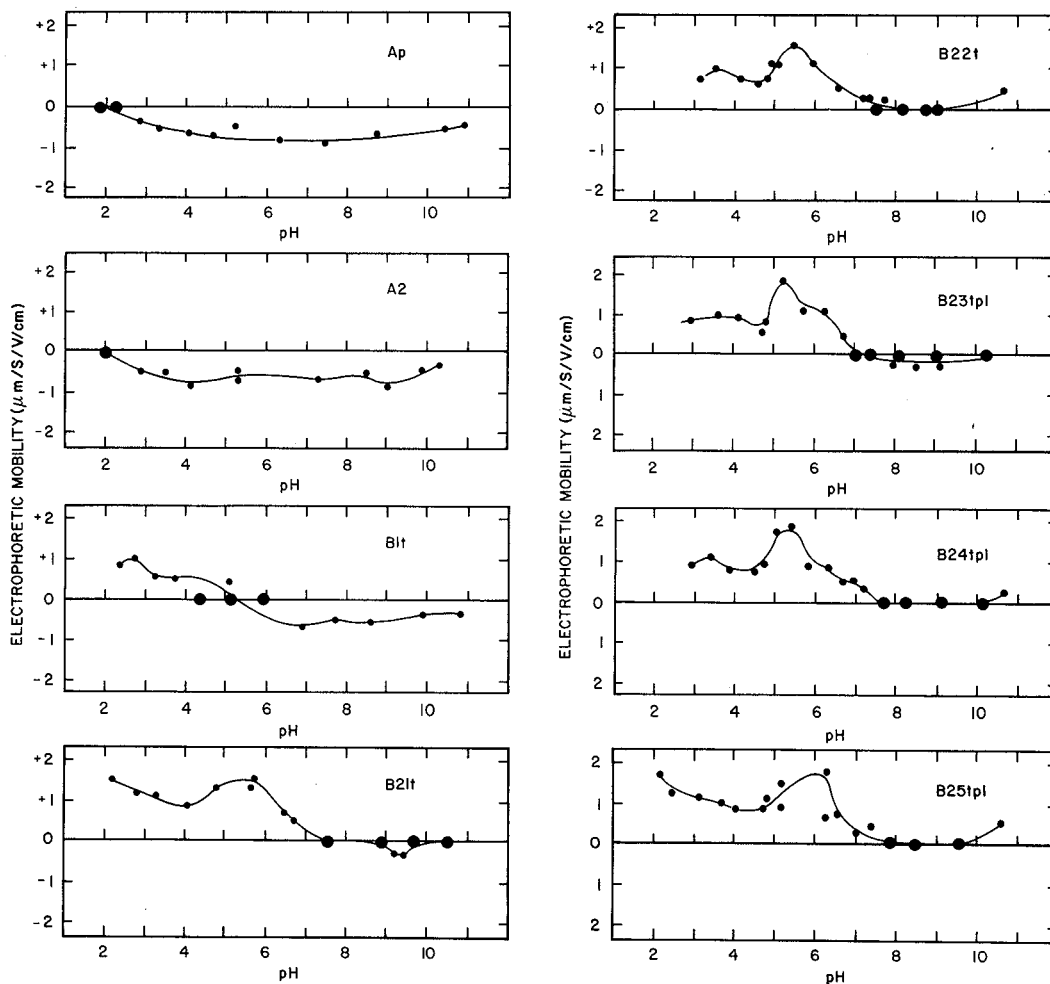


FIG. 1. The pH-dependent electrokinetic behavior of: (left) the Ap, A2, B1t, and B21t horizons; (right) the B22t, B23tpl, B24tpl, and B25tpl horizons. Enlarged data points on the pH axis indicate pH at which no measurable movement was observed or particles moving in both directions.

TABLE 2
Comparison of ZPC with Fe-oxide and OM content
of the soil profile

Horizon	ZPC ^a	Fe oxides, %	Organic matter, %
Ap	2.0	0.23	1.28
A2	2.0	0.26	0.23
B1t	5.1	1.24	0.34
B21t	7.5	1.35	0.30
B22t	7.5	1.80	0.23
B23tpl	7.1	2.68	0.16
B24tpl	7.7	3.30	0.16
B25tpl	7.9	3.60	0.16

^a Zero point of charge or the least alkaline pH at which electroneutral conditions were observed.

dance of minerals with characteristically low ZPC values, namely, silica and feldspars. The A horizons are high in sand (Table 1), and, in a previous study, Sparks et al. (1980b) found substantial levels of K-feldspars in the Dothan soil, particularly in the Ap and A2 horizons (11.3 and 8.2 meq/100 g, respectively). Thus, the A horizons should have low ZPC values, because pure silica has a value of 2.0 (Li and DeBruyn 1966; Parks 1967; Huang et al. 1977) and feldspars range from less than 2 to 2.4 (Warren and Kitchener 1972).

Perhaps the most striking feature of these data is the gradual increase in ZPC with soil

profile depth, the most abrupt increase occurring in the transition from the A2 to the B1t horizons. This finding, when interpreted on the basis of the data in Table 2, demonstrated the importance of mineralogical composition in determining soil charge characteristics. As multicomponent mixtures, soils must have surface charge properties that reflect the overall surface characteristics of the mineral suite of which they are composed. This has been demonstrated for binary (aluminum/silicon) systems (Smolik et al. 1966) and can be extended to more complex mixtures (Parks 1967). Because sesquioxides generally have ZPC values in the neutral [Fe_3O_4 (6.5); $\gamma\text{-Fe}_2\text{O}_3$ (6.7)] or alkaline [$\alpha\text{-Al}_2\text{O}_3$ (9.1); amorphous $\text{Fe}(\text{OH})_3$ (8.5)] pH range (Stumm and Morgan 1970), it would be expected that soils with substantial sesquioxide contents should exhibit higher ZPC values. A relationship between elevated ZPCs and increased sesquioxide content has been observed for some soils (van Raij and Peech 1972; Hendershot and Lavkulich 1979).

In this study, the gradual increase in ZPC with depth is a reflection of the increasing Fe-oxide content (Table 2). The Ap and A2 horizons, with nearly identical Fe values, have the same ZPC (ca. 2). A large increase in ZPC (to 5.1) was observed when the Fe content increased substantially in the B1t horizon and increased further to about 7 to 8 for the B2t horizons.

Compelling evidence for the crucial role of Fe oxides in determining ZPC in these soils is shown in Fig. 2, which depicts the effect of Fe removal on the EM-pH behavior of the B25tpl horizon. It can be noted that the removal of the iron

oxide fraction completely reversed the sign of the surface charge and depressed the ZPC to a value similar to that of the surface horizons. Removal of Fe leaves basically a silicate structure, and SiO_2 , as noted, characteristically has a low ZPC of about pH 2.

The data obtained here tend to confirm the hypothesis expressed in the past (Toth 1937), and restated more recently (Jenne 1968), that Fe-hydrous oxides in soils occur principally as deposited coatings on the silicate soil components, rather than as discrete crystallized entities. Iron contents of 1 to 3% in the soil were observed to have a marked elevating effect on ZPC. The disproportionate influence of Fe content on ZPC suggests that the iron compounds exist as thin layers surrounding a core of silicate material. Surface adsorption/precipitation of one phase onto another solid often imparts to the latter surface properties characteristic of the former. Tewari and Lee (1975) found that Al_2O_3 and ZrO_2 , upon adsorption/precipitation of cobalt (II) from aqueous solution, exhibited x-ray photoelectron spectral and electrophoretic mobility behavior that corresponded closely to that of $\text{Co}(\text{OH})_2$. In this study, the soil particles attained ZPC values characteristic of ferric oxides and hydroxides (ca. 6.5 to 8.5). Such a phenomenon is possible only if the Fe minerals coat the soil particles to the extent that the soil colloids lose their interfacial identity and behave in the bulk solution as Fe-hydrous oxides.

Specific adsorption of Ca^{2+}

All the B2t horizon samples exhibited unusual electrokinetic behavior in the alkaline pH re-

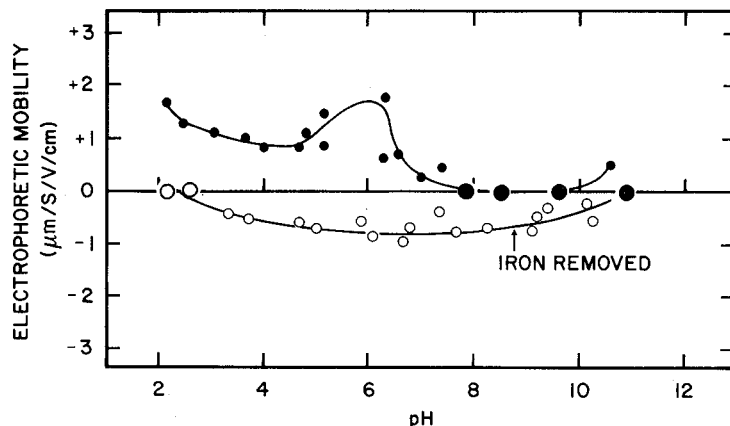


FIG. 2. Effect of removing iron from the B25tpl soil on the electrokinetic behavior.

gion: it was impossible to precisely identify a unique ZPC, for zero electrophoretic mobility was observed over a range of pH values. This behavior is most readily accounted for by the specific adsorption of Ca^{2+} from the background electrolyte. Adsorption is termed *specific* when it occurs in response to adsorbate-adsorbent interactions other than electrostatic attraction. This specific adsorption of Ca^{2+} is demonstrated in Fig. 3, which compared the EM-pH behavior of the B25tpl soil horizon using CaCl_2 and NaCl as electrolytes at an identical ionic strength (0.03 M). In NaCl , the EM at the alkaline pH values was clearly negative, and a well-defined ZPC was established. The reduction in ZPC from about 7.9 (in CaCl_2) to 6.2 (in NaCl) is in accord with the fact that specific adsorption of cationic species (e.g., Ca^{2+}) tends to shift the observed ZPC to higher pH values (Stumm and Morgan 1970).

Specific interaction of alkaline-earth cations with sesquioxide surfaces has been documented (Breeuwsma and Lyklema 1971; Huang and Stumm 1973; Breeuwsma and Lyklema 1973). In their study of the hematite ($\alpha\text{-Fe}_2\text{O}_3$)-aqueous solution interface, Breeuwsma and Lyklema (1971, 1973) found that many divalent cations were specifically adsorbed and that Ca^{2+} at concentrations as low as 5×10^{-4} M caused a two pH unit shift in the point of zero charge.

The question arises as to which electrolyte is most appropriate for ZPC determinations. To avoid specific adsorption, the electrolyte should comprise particular ions; for example, some investigators feel that KClO_4 (Dumont et al. 1976)

and KNO_3 (Mekaru and Uehara 1972) are suitable. However, values obtained under such conditions may be an inaccurate guide to behavior in the soil solution. A 0.01 M CaCl_2 electrolyte medium was chosen for this study, because it is commonly used to simulate soil solution and, on the basis of Table 1, is an appropriate choice for these soils in particular. Additionally, it allows investigation over a wide pH range (2 to 12) while maintaining constant ionic strength.

ZPC depth variations

The ZPC of the soils versus the midpoint depth of the horizon from which they were taken is plotted in Fig. 4. The surface horizons are characterized by low ZPC values (~ 2). The ZPC increased rapidly in the lower horizons, with the B2 soils exhibiting ZPC values in the 7 to 8 range. Therefore, under typical pH conditions encountered in soil systems, a certain critical depth exists at which the pH-dependent net surface charge switches from negative to positive. This critical depth appears to be about 30 to 50 cm below the surface, depending on the existing solution hydrogen-ion concentration.

The existence of an appreciable anion exchange capacity will affect transport through the soil column of certain electronegative species of agronomic importance. The well-documented affinity of Fe oxides for PO_4^{3-} and SO_4^{2-} is a manifestation of specific adsorption processes (Schwertmann and Taylor 1977), the retention of these anions not being dependent on an electrostatically favorable environment. Nevertheless, a favorable coulombic free energy of ad-

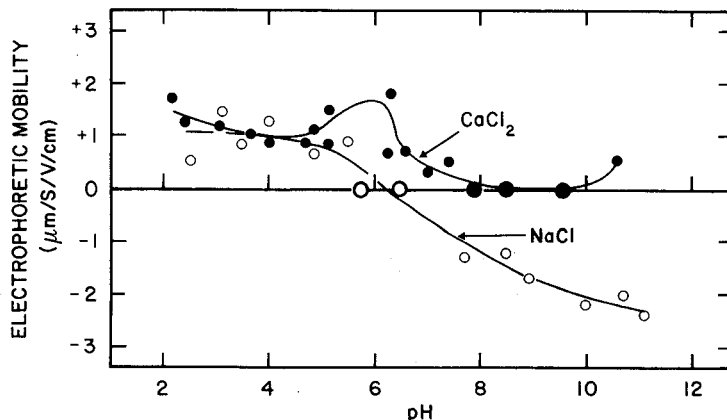


FIG. 3. Influence of nature of electrolyte on electrokinetic behavior of the B25tpl soil. Both systems had an ionic strength of 0.03 M.

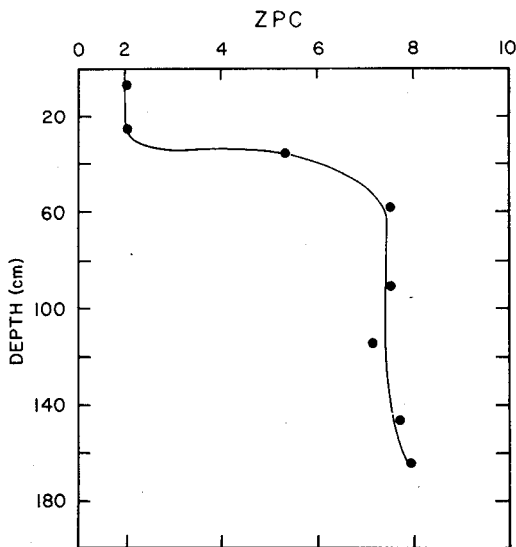


FIG. 4. Zero point of charge (ZPC) as a function of horizon midpoint depth.

sorption due to a positive surface charge will result in even stronger retention of these multivalent anions. Thus, the lower horizons of the Dothan profile should bind PO_4^{3-} and SO_4^{2-} rather tightly.

Nitrate retention, on the other hand, is apparently via nonspecific adsorption only (Mekaru and Uehara 1972). Thus, the prevailing negative surface charge exhibited by most soils allows NO_3^- to leach to groundwater where it presents a potential health hazard. At typical field pH, the lower horizons in this profile should accumulate all anions, including NO_3^- , as counterions in the diffuse double layer in response to the electropositive surface charge. Accordingly, the risk of groundwater NO_3^- pollution through overfertilization could be reduced somewhat compared with soils that carry a net negative charge. Such soils would also be ideally suited as disposal sites for domestic wastewaters, sludges, and nitrogenous agricultural residues.

CONCLUSIONS

Using electrophoresis to establish the charge characteristics of a soil profile from the Atlantic Coastal Plain region, we found that the surface horizons had low ZPC values (~ 2) and the B2t horizons exhibited ZPC values in the 7 to 8 range. The abrupt rise in ZPC in the B1t horizon, accompanied by a sizeable increase in iron content, suggested that the appreciable change in ZPC with soil depth is primarily a reflection of

the variation in Fe-oxide content. A shift in the ZPC of the B25t soil from 7.9 to 2.3, as a result of Fe removal, provides compelling supportive evidence.

Electrochemical behavioral similarities between the soils with iron concentrations of only 1 to 3% and pure Fe-hydrous oxides support the belief that soil iron exists primarily as surface coatings, rather than discrete mineral entities. Accordingly, the soil particles exhibited surface behavior typical of iron oxides, as exemplified by specific adsorption of Ca^{2+} .

At some depth in the profile, the sign of the soil surface charge changes from net negative to net positive, indicating that, at the same depth, the pH-dependent exchange capacity becomes anionic rather than cationic. Movement of anionic plant nutrients will be affected. Reduced potential for groundwater pollution resulting from NO_3^- leaching subsequent to fertilization or land application of nitrogenous waste materials can be expected in these soils.

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