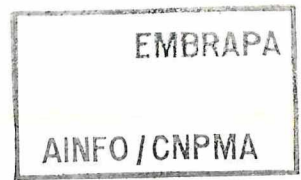


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Effects of Liming, Green Manuring, and Phosphate Addition on Electrochemical Attributes of an Oxisol from Central Brazil

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ABSTRACT *sk*

Highly weathered tropical soils are characterized by having a predominantly variable charge. Many management practices commonly used in the exploitation of these soils (e.g., liming, phosphate application, and manuring) are known to modify their electrical charge and the sorption/desorption behavior of cations and anions. This process is, at least, partially governed by the charges existing in the soil system. Available information on this subject comes mainly from short-term laboratory and greenhouse experiments. There is a lack of data regarding the cumulative and long-term effects of those practices used at farm-scale levels and on the dynamics and availability of nutrients to the plants under field conditions. In the present work, changes in some electrochemical attributes of a variable charge soil (Oxisol) were studied, as influenced by treatments with phosphate + green manure (*Cajanus cajan*), phosphate + lime, and phosphate + lime + green manure, applied

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during a six-year period. In this period, rice, bean, wheat, or corn, were grown in seventeen successive crops. Phosphate (total 334 ppm P) and phosphate + lime (total 5.5 t ha⁻¹) were shown to increase net electric charge and soil cation exchange capacity (CEC) at the field pH, and not to affect zero point of charge (ZPC), CEC at pH 7.0, or anion exchange capacity (AEC) of the soil at the field pH. The effects of phosphate + lime were more pronounced than those of phosphate alone. Green manure (total 16 t ha⁻¹ dry matter), associated to crop residues and phosphate or phosphate + lime, did not influence electrochemical properties.

INTRODUCTION

Highly weathered soils of tropical region, as the Oxisol order, present variable charge due to the predominance in its colloidal fraction of iron (Fe) and aluminum (Al) oxides and hydroxides and low activity clays like kaolinite. These minerals are amphoteric and their surface electrical charges are controlled mainly by adsorption and desorption of H⁺ and OH⁻ (Raij and Peech, 1972). In these soils, positive and negative charges coexist in natural conditions. Once the relative distribution of those charges may vary intensely with pH and ionic concentration of the soil solution, any external component introduced in the system that modify those attributes will change the soil anion and cation retention capacity.

One important parameter used to describe the electrochemical behavior of variable charge soil is the point of zero charge (Uehara and Gillman, 1980). Although a property relatively stable, specific adsorption of anion (Uehara and Keng, 1975) and the soil organic matter (Raij and Peech, 1972; Moraes et al., 1976) may significantly modify its value.

Tropical soils frequently have to be limed in order to decrease the Al toxicity, add calcium (Ca), and increase crop yields. Several authors (Raij and Peech, 1972; Smyth and Sanchez, 1980; Bolan et al., 1988; Naidu et al., 1990) working on different variable charge soils, verified that the net negative charge increased as pH increased due to lime. Some of them (Raij and Peech, 1972; Naidu et al., 1990) indicated that the increase in negative and decrease in positive charge was not proportional.

There is generalized phosphorus deficiency in the tropics in which phosphorus (P) fertilization is an obligatory practice to obtain good grain yields. In addition to its function as a nutrient, phosphate applied in these very weathered soils may increase soil CEC (Mekaru and Uehara, 1972; Wann and Uehara, 1978; Gillman and Fox, 1980) due to the displacement of hydroxyls and/or water molecules which are coordinated to Fe or Al of the sesquioxides surface, thereby increasing their negative charge. Although the increase in CEC due to phosphate application to those soils may be significant, fertilizer applications are generally not economical (Mekaru and Uehara, 1972; Gillman and Fox, 1980). On the other hand, P-

adsorption may decrease the anion exchange capacity due to reduction of the positive charge of the soil colloids.

Organic matter is the main component responsible for negative charge development in soils with variable charge. It may represent up to 90% of the total soil CEC (Raij, 1969). Besides its contribution to the increase in CEC it also influences the soil ZPC (Raij and Peech, 1972) tending to displace it to lower values.

The objective of the present work was to study the influence of liming, phosphate application, and green manuring on some electrochemical attributes of an Oxisol in actual agricultural field conditions.

MATERIALS AND METHODS

Soil Samples

The soil used in this study was an Oxisol (clayey dark red latosol) located in Santo Antonio do Goiás County, in the Goiás State, Brazil. It is geographically and economically representative of the Cerrado region.

Samples from depths of 0-20, 20-40, and 40-60 cm were collected in April 1991 from field experiment, conducted from November 1982 through July 1989. Samples from each treatment and layer were composed of eight subsamples (two for each replicate) collected in small pits opened in locations chosen randomly inside each plot. The subsamples were air dried and passed through a 2-mm sieve. During that period, rice, bean, wheat, or corn, were grown as seventeen successive crops. From July 1989 through April 1991 the plots were fallowed. The plots selected in the experiment for this study were check (T), phosphate (P), phosphate + green manure (*Cajanus cajan*) (Pgm), phosphate + lime (Pca), and phosphate + lime + green manure (Pcgm). Phosphate fertilization corresponded to 90 kg of P_2O_5 from MAP in each cultivation period (1,500 kg ha^{-1} of P_2O_5 for the entire six-year period). It was applied as 5.5 t ha^{-1} dolomitic limestone divided in one 2.5 t ha^{-1} rate in 1982 before the first growing period and another rate of 3.0 t ha^{-1} in 1985 between the ninth and tenth cropping period. Lime was broadcast and plow incorporated. Green manure was applied at a rate of 16 t ha^{-1} dry weight.

Electrochemical Attributes

The soil ZPC of the samples was measured using the potentiometric titration curves essentially as described by Raij and Peech (1972). The net electric charge at pH different from the PZC was estimated by interpolation of the titration curve according to the desired electrolyte concentration. The chosen concentration was as near as the ionic strength of the soil solution, estimated here by the Gillman and Bell (1978) procedure. The method by Gillman (1979) was chosen for the determination of CEC and AEC at natural soil pH condition and CEC at pH 7.0 was measured using 1N Ca and sodium acetate at pH 7.0 (Camargo et al., 1986).

TABLE 1. Zero point of charge of the several soil depths affected by treatments.

| Soil depth (cm) | ZPC | | | | |
|--------------------|-------------------------|-----|-----|-----|-------|
| | Treatments ^a | | | | |
| | Check | P | Pgm | Pca | Pcagm |
| 0-20 | 3.7 | 3.5 | 3.5 | 3.5 | 3.5 |
| 20-40 | 3.8 | 3.8 | 3.7 | 3.8 | 3.8 |
| 40-60 | 4.6 | 4.5 | 4.3 | 4.4 | 4.4 |

^aP=phosphate (1,500 kg ha⁻¹, P₂O₅), Pgm=phosphate plus green manure (16 t ha⁻¹ dry matter), Pca=phosphate plus lime (5.5 t ha⁻¹), Pcagm=phosphate plus lime plus green manure.

RESULTS AND DISCUSSION

Point of Zero Charge

Table 1 shows the values of ZPC for the three depths and five treatments obtained from the crossing point of the titration curves. These values are similar to those obtained for other Brazilian soils (Raj and Peech, 1972; Moraes et al., 1976). The ZPC increased with depth from 3.7/3.8 to 4.3/4.6 in the 0-20- and 20-40-cm and 40-60-cm depths, respectively. That increase was due to the decrease of the organic matter content once there is a negative correlation between those two attributes (Siqueira et al., 1990). Apparently there were no significant differences among treatments in each layer, which shows that liming, phosphate fertilization, and green manuring at the applications used did not affect the ZPC value in the Oxisol studied. This observation was different from the data obtained by Wann and Uehara (1978) and Laverdiere (1982) who found decreasing values of ZPC with phosphate application. One cause of this difference may have been that in those studies, P was applied both in the laboratory and greenhouse experiments at one time and ZPC was measured after a short period of time. In the present study, a low amount of P (55.7 ppm) was applied each year during the six years of the experiment and ZPC was measured following a 21 months fallow period after the end of the experiment. It should be stressed that Wann and Uehara (1978) did not find any change in the ZPC at low P concentration which could be compared to the present case.

Green manure application also did not alter the ZPC (Table 1). Although organic matter tends to decrease ZPC, there is no certainty that increasing SOM through management practices may decrease the ZPC (Sanchez, 1976). Siqueira et al. (1990) observed no correlation between organic carbon added in an Oxisol and

TABLE 2. Net electric charge of the soil samples in the five treatments, at three pH values.

| pH | Net electric charge | | | | |
|----------|--|-------|-------|-------|-------|
| | Treatments ^a | | | | |
| | Check | P | Pgm | Pca | Pcagm |
| | ----- cmol _c kg ⁻¹ ----- | | | | |
| | 0-20 cm | | | | |
| 4.5 | -0.2 | -0.3 | -0.4 | -0.4 | -0.4 |
| field pH | -0.4 | -0.7 | -0.8 | -0.9 | -0.9 |
| | (5.3) ^b | (5.4) | (5.6) | (5.8) | (5.9) |
| 6.5 | -1.4 | -1.8 | -1.7 | -1.6 | -1.5 |
| | 20-40 cm | | | | |
| 4.5 | -0.4 | -0.4 | -0.4 | -0.3 | -0.3 |
| field pH | -0.7 | -0.6 | -0.6 | -0.5 | -0.6 |
| | (5.2) | (5.3) | (5.1) | (5.5) | (5.7) |
| 6.5 | -1.2 | -1.1 | -1.2 | -1.0 | -1.0 |
| | 40-60 cm | | | | |
| 4.5 | +0.1 | 0.0 | 0.0 | -0.1 | 0.0 |
| field pH | -0.2 | -0.2 | -0.2 | -0.2 | -0.3 |
| | (5.3) | (5.3) | (5.5) | (5.4) | (5.6) |
| 6.5 | -0.3 | -0.5 | -0.5 | -0.5 | -0.5 |

^aP=phosphate (1,500 kg ha⁻¹, P₂O₅), Pgm=phosphate plus green manure (16 t ha⁻¹ dry matter), Pca=phosphate plus lime (5.5 t ha⁻¹), Pcagm=phosphate plus lime plus green manure.

^bFigures in brackets represent the pH of the soil samples taken at field conditions for each treatment and depth.

the ZPC and concluded that adding green manure or crop residue did not affect the ZPC for several years.

Net Electric Charge

Once the ionic strength of the soil solution varied from $2.11 \times 10^{-4} \text{M}$ in the check treatment in the 40-60-cm layer to $10.49 \times 10^{-4} \text{M}$ in the Pcagm treatment in the 0-20-cm layer, the 0.001 mol L^{-1} in KCl titration curve was used to evaluate the net electric charge (Table 2). The charges were predominantly negative. Just in the 40-60-cm layer at pH 4.5 the net charge oscillated around $0.00 \text{ cmol}_c \text{ kg}^{-1}$ indicating a balance between net negative and net positive charge. There was a trend of decreasing negative charge as depth increased independently of the pH and probably related to SOM decrease. It may also be observed that net negative

TABLE 3. The cation exchange capacity and anion exchange capacity at field soil pH (CEC nat., AEC nat.), and cation exchange capacity at pH 7.0 (CEC 7.0) for the three soil depths and five treatments.

| Treatments ^a | CEC nat. | CEC 7.0 | AEC nat. |
|--|----------|---------|----------|
| ----- cmol _c kg ⁻¹ ----- | | | |
| 0-20 cm | | | |
| Check | 4.5 | 7.8 | 0.16 |
| P | 4.8 | 8.2 | 0.14 |
| Pgm | 4.6 | 8.3 | 0.16 |
| Pca | 5.6 | 7.8 | 0.15 |
| Pcagm | 5.5 | 8.0 | 0.20 |
| 20-40 cm | | | |
| Check | 4.4 | 6.6 | 0.30 |
| P | 4.4 | 6.7 | 0.24 |
| Pgm | 4.5 | 6.6 | 0.26 |
| Pca | 4.6 | 6.4 | 0.22 |
| Pcagm | 4.7 | 6.5 | 0.22 |
| 40-60 cm | | | |
| Check | 4.4 | 4.6 | 0.24 |
| P | 4.3 | 4.8 | 0.28 |
| Pgm | 4.4 | 4.7 | 0.24 |
| Pca | 4.3 | 4.8 | 0.27 |
| Pcagm | 4.4 | 4.6 | 0.27 |

^aP=phosphate (1,500 kg/ha¹, P₂O₅), Pgm=phosphate plus green manure (16 t ha⁻¹ dry matter), Pca=phosphate plus lime (5.5 t ha⁻¹), Pcagm=phosphate plus lime plus green manure.

charge increased with pH and decreased from the field pH in each layer. This demonstrated a dependence of the CEC to pH variations.

All treatments increased the negative charge 0.4 cmol_c kg⁻¹ in average compared to the control. Although this is a small value for this type of low activity soil, it is significant, because it represents an increase of 100%. Smyth and Sanchez (1980) obtained similar results with a similar soil in a greenhouse and laboratory experiment. As in our study, they verified a more significant increase when P fertilization was associated with liming. The green manure seems not to affect the negative charges.

Ion Exchange Capacity

The CEC and AEC at the soil field pH and at pH 7.0 is recorded in Table 3. Parfitt (1980) described an increase in 50% of CEC when liming a variable charge

soil from pH 5 to 6. A similar trend was demonstrated here for the 0-20-cm depth increment, where an increase in 0.5 pH units resulted in a $0.7 \text{ cmol}_c \text{ kg}^{-1}$ increase in CEC. Phosphate fertilization alone showed little tendency to increase CEC at field pH, even though the values found were close to those obtained by Sanchez and Uehara (1980). They found CEC values of $0.1\text{-}0.2 \text{ cmol}_c \text{ kg}^{-1}$ per $100 \mu\text{g g}^{-1}$ of P added. The CEC at field pH was not affected by the treatments in the 20-40- and 40-60-cm depths nor was the CEC at pH 7.0 affected by treatments and depths studied.

The AEC at the original soil pH varied from $0.14 \text{ cmol}_c \text{ kg}^{-1}$ in the P treatment in the 0-20-cm depth to $0.30 \text{ cmol}_c \text{ kg}^{-1}$ in the check in the 20-40-cm depth. This variation is comparable to those obtained by Smyth and Sanchez (1980) for a similar Oxisol in the Brazil Central Plateau. Although the differences may be great in a relative comparison they are small in absolute values and may not reflect the actual differences among the treatments. The intrinsic difficulties of AEC determination resulted in considerable errors at low values. In this study, no treatment of any considered significantly affected the soil AEC.

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Effect of Treated Sewage Water on the Concentration of Certain Nutrient Elements in Date Palm Leaves and Fruits

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ABSTRACT

Leaflet and fruit samples were collected from 9-year old palms irrigated with potable water and treated sewage water from two locations (the University and the city sewage effluent plant). After drying, ashing, and dissolution of ash by HCl, calcium (Ca), and magnesium (Mg) concentrations were determined by atomic absorption photometry; sodium (Na), and potassium (K) by flame spectrophotometry and chlorine (Cl) by titration. Results of the present study were then compared with those of 1993. Unlike the 1993 results, K, Ca, Mg, and Na concentrations did not show any significant differences in leaves or fruits. Potassium, Ca, and Mg in leaves and fruits irrigated with three types of water in 1995 showed higher concentrations than in 1993. Sodium was lower in leaves and fruits during 1995 than 1993 when treated sewage water was used, but with potable water it was higher in leaves and lower in fruits. The increase in K, Ca, and Mg and the reduction in Na were



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