

Plant Residues: Short Term Effect on Sulphate, Borate, Zinc and Copper Adsorption by an Acid Oxisol

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ABSTRACT

Laboratory experiments were carried out to examine the effects of plant residues on Cu, Zn, B and S adsorption by an acidic oxisol. The plant residues were: black oats (*Avena strigosa*), oil seed radish (*Raphanus sativus*), velvet beans (*Stizolobium cinereum*), and pigeon pea (*Cajanus cajan*) collected at flowering stage. Plant residues increased Cu and Zn adsorptions and decreased B and S adsorptions. The results indicated that for short term effect plant residues decreased the availabilities of Cu and Zn through metal organic complex reactions and increased availabilities of S and B through competition with organic anions by the adsorption sites on soil.

Key words: Green manure, cover crop, micronutrient, soil sorption

INTRODUCTION

Fresh plant residues have water-soluble organic compounds of low molecular weight with high capacity of forming stable complexes with cations and preventing inorganic anion adsorption by acid soils. The water soluble organic compounds contain one or more carboxyl (COOH) and phenolic (OH) functional groups that possess negative charge when fully dissociated. Due to the negative charge associated with these groups, the organic acids can become sorbed to the positive charges on the soil's solid phase or forming complexes with metallic cations in solution.

It is well established that pure organic acids prevent inorganic anion adsorption (Appelt et al., 1975; Traina et al., 1986; Evans and Anderson, 1990). These authors concluded that the competition for adsorption sites was the main mechanism for the effect of organic acids on inorganic anion adsorption. Organic acids have also the capacity to

form complexes with metals in soil solution (Harter and Naidu, 1995). Based on the stability constants of organic acid-metal complexes (Martell and Smith, 1989) it can be established that organic acids have high affinity for Zn^{2+} and Cu^{2+} . These studies on metal organic complexes were done with pure organic acid solutions. There has been no direct study comparing the effect of plant residues on the sorption/desorption of cations and anions by soils.

The objective of the present study was to examine the influence of black oats, oil seed radish, velvet beans, and pigeon pea residues on the adsorption of sulphate, borate, zinc and copper by an acidic oxisol.

MATERIAL AND METHODS

Soil samples taken from the A horizon were air-dried, ground, and passed through a 2 mm sieve. The soil had an original pH measured in $CaCl_2$

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slurry with a value of 4.2; exchangeable Ca, Mg, K and Al contents of 2.4, 0.92, 0.23 and 0.90 Cmolc dm⁻³, respectively, and total organic carbon content of 17 g kg⁻¹. The clay, silt, and sand contents were 750, 100, and 150 g kg⁻¹, respectively. Plant materials were: black oats (*Avena strigosa*), oil seed radish (*Raphanus*

sativus), velvet beans (*Stizolobium cinereum*), and pigeon pea (*Cajanus cajan*). Plant materials were collected at flowering stage, dried at 65°C for 48 h, ground to pass 1 mm sieve, stored in plastic bags, and analyzed (Table 1). Plant materials were added to the soil sample at a rate of 1% (w/w).

Table 1 - Chemical composition of plant residues.

| Element | Plant residue | | | |
|---------------------------|---------------|--------|--------|--------|
| | Oats | Radish | Velvet | Pigeon |
| N (g kg ⁻¹) | 29.6 | 29.4 | 25.6 | 29.0 |
| P (g kg ⁻¹) | 4.6 | 5.0 | 1.8 | 2.3 |
| K (g kg ⁻¹) | 35.2 | 30.1 | 44.8 | 12.6 |
| Ca (g kg ⁻¹) | 6.0 | 22.3 | 7.8 | 10.0 |
| Mg (g kg ⁻¹) | 2.0 | 2.8 | 2.8 | 2.6 |
| Cu (mg kg ⁻¹) | 10.5 | 9.7 | 20.7 | 18.0 |
| Zn (mg kg ⁻¹) | 39.4 | 39.7 | 66.9 | 26.5 |
| B (mg kg ⁻¹) | 7.7 | 28.4 | 38.8 | 21.1 |
| Mn (mg kg ⁻¹) | 286.4 | 65.8 | 582.3 | 87.2 |

Zinc, copper, boron, and sulphate solutions were prepared from ZnSO₄·7H₂O, CuCl₂·2H₂O, Na₂B₄O₇·10H₂O, and K₂SO₄, respectively, at the following concentrations: Zn 4, 8, 16, 32, and 64 mg kg⁻¹; Cu 2, 4, 8, 16, and 32 mg kg⁻¹; B 1, 2, 5, 10, and 20 mg kg⁻¹; and S 10, 20, 50, 100, and 200 mg kg⁻¹. Sorptions of Zn, Cu, B and S in the presence and absence of plant residues were measured by shaking duplicates 5 g samples of soil with 5 ml solutions containing appropriate amounts of each element, in 50 ml centrifuge tubes. Amended soil samples were incubated for 5 d. Then, the extractant solutions were added, shaken, centrifuged at 2500 rpm for 10 minutes, filtered, and the concentrations of Zn, Cu, B, and S were determined by inductively coupled plasma (ICP) spectroscopy. The extractant solutions were DTPA for Zn and Cu (Raij et al., 1996), 0.05 mol L⁻¹ HCl for B (Correa et al., 1985) and 0.01 mol L⁻¹ Ca(H₂PO₄)₂·2H₂O for S (Raij et al., 1996). Sorbed Zn, Cu, B and S were calculated as the difference between the amount added and the amount remaining in the extractant solution after shaking. All treatments were performed in triplicate, and standard error of the treatment means were calculated.

RESULTS AND DISCUSSION

At least for short term experiment, all plant residues increased Cu²⁺ and Zn²⁺ adsorptions by the soil (Fig. 1 and 2). Due to the negative charges associated with carboxyl and phenolic functional groups of the organic compounds, Cu²⁺ and Zn²⁺ were readily sorbed on the organic phase. The acidic function groups of the organic compounds presented acidic properties in which the H⁺ ions can be replaced under certain circumstances by metallic ions, such as Cu²⁺ and Zn²⁺ forming coordinated bounds.

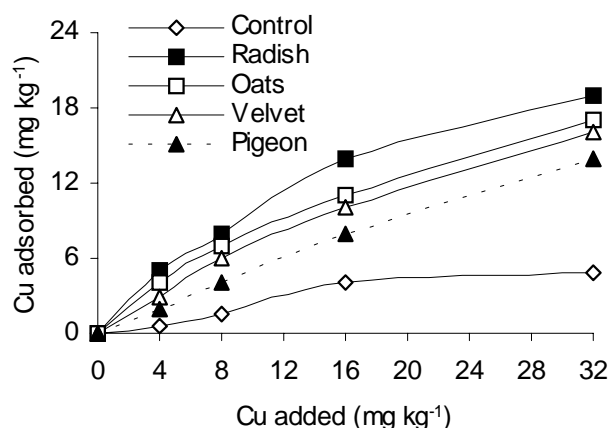


Figure 1 - Effect of plant residue on Cu sorption.

The greater adsorption of Cu^{2+} in relation to Zn^{2+} was probably due to higher stability constant of the Cu^{2+} -organic forms (Martell and Smith, 1989). The degree of metal sorption, however, depended on the particular plant species. The effect of plant residue on Cu^{2+} and Zn^{2+} sorptions followed the order: oil seed radish > black oats > velvet beans > pigeon pea. These results indicated that for short term effect plant residues could decrease the availability of Cu^{2+} and Zn^{2+} in soil through metal organic complexes due to the high stability constants of Cu^{2+} and Zn^{2+} with organic anions (Lide, 1992). Thus in marginal cases it might be possible to alleviate Cu and Zn toxicities by proper use of plant residues.

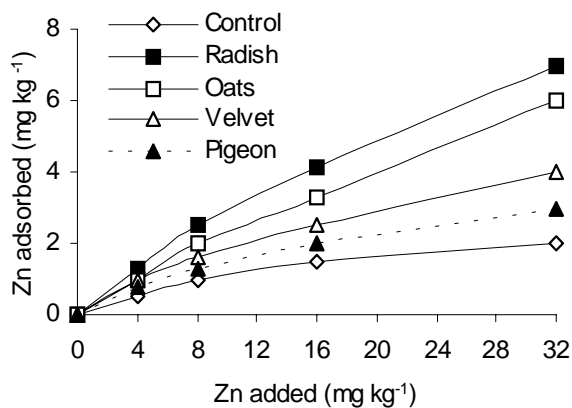


Figure 2 - Effect of plant residue on Zn sorption.

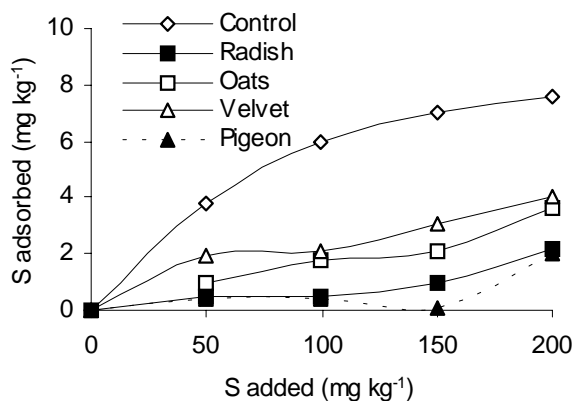


Figure 3 - Effect of plant residue on S sorption.

The higher adsorption capacity of oil seed radish and black oats by Cu^{2+} and Zn^{2+} was probably due

to their higher amounts of acidic functional groups (Cassiolato et al., 2001) and to their higher proportion of forming stable complexes with cations (Franchini et al., 2001). It was unlikely that organic residues formed precipitates with Cu^{2+} and Zn^{2+} in soil.

On the other hand the presence of plant residue decreased the adsorption of S and B by soil (Fig. 3 and 4). The decrease in adsorption was higher for B than for S, probably due to weaker competition of borates than sulphates with organic anions by the adsorption sites. Various reasons have been proposed for the decrease in the adsorption of anions in the presence of organics.

Organic anions released from the plant materials competed with inorganic anions such as borates and sulphates for the positive adsorption sites on soil and thereby decreasing S and B adsorptions. Typically plant residues contain many organic acids with low molecular weight varying in chain length (Franchini et al., 2001) which can carry negative charges, thereby allowing the competition with inorganic anions with soil matrix. Studies with inorganic and organic anions have shown that sorption trend was phosphate > oxalate > malate > sulphate > acetate (Jones and Brassington, 1998). It was probably that these anions share similar sorption sites on soil and were all capable of preventing the sorptions of added S and B. Thus plant residues could improve S and B availabilities by decreasing their sorptions in soil and consequently ameliorating S and B nutritions.

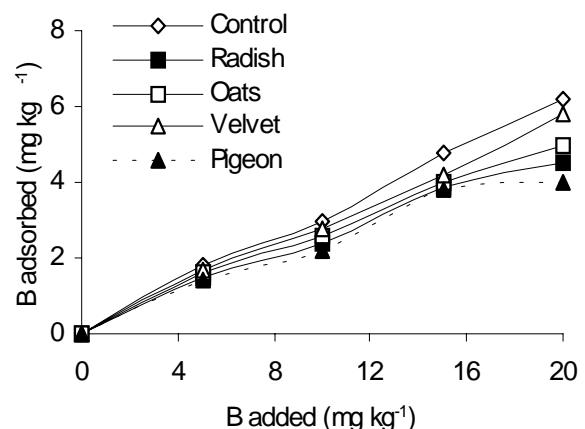


Figure 4 - Effect of plant residue on B sorption.

CONCLUSIONS

Plant residues decreased the availabilities of Cu²⁺ and Zn²⁺ through metal organic complex reactions and increased the availabilities of S and B through competition with organic anions by the soil adsorption sites.

RESUMO

Resíduos vegetais frescos possuem compostos orgânicos hidrossolúveis de baixo peso molecular com alta capacidade de complexação com cátions e de competição na adsorção de ânions em solos ácidos. Foram conduzidos experimentos de laboratório para avaliar os efeitos de resíduos de aveia preta (*Avena strigosa*), nabo forrageiro (*Raphanus sativus*), mucuna anã (*Stizolobium cinereum*) e guandu (*Cajanus cajan*), coletados em pleno florescimento, na adsorção de Cu, Zn, B e S por um latossolo ácido. Os resíduos vegetais aumentaram a adsorção de Cu e Zn e diminuíram as de B e S. Os resultados indicaram que as transformações rápidas dos compostos orgânicos dos resíduos vegetais diminuem a disponibilidade de Cu e Zn através de reações de complexação organo-metálica e aumentam as de S e B através de competição com ânions orgânicos pelos sítios de adsorção do solo.

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