SIGN-OF-CHARGE OF SPECIES OF Cu, Cd AND Zn EXTRACTED FROM SEWAGE SLUDGE, AND EFFECT OF PLANTS

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SUMMARY

Sewage sludge, obtained from the Back River Wastewater Treatment Plant, Baltimore, Maryland, in 1970, was stored either moist or air-dried for 5 years. Aqueous extracts of sludge were obtained and leached through columns containing either cation, anion, or mixed resins, with the pH adjusted to equal that of the extract. Analysis of the column leachates for Zn, Cd, and Cu was used to calculate concentrations of the various charged metal species. For Zn, between 84 and 92% of the species were cationic regardless of moisture conditions during storage; for Cd, moist storage yielded 83% amphoteric, and air dry storage 87% cationic species; for Cu, moist storage yielded 50% cationic and 30% amphoteric species, while air-dry storage yielded 16% cationic and 72% amphoteric species.

Soybeans (Glycine max, var. Delmar) were exposed for 48 h to aerated aqueous extracts of Cu-enriched sludge. About 68% of $M^2$, 55% of $M^+$, 83% of $M^-$, and 100% of $M^0$ remained in the extracts after the exposure.

INTRODUCTION

The strength of associations between organic matter and heavy metals depends on the type of binding sites, their abundance and distribution, the degree of their saturation with counter ions, the species of heavy metal, and the pH and ionic strength of the interstitial equilibrium solution. Although the structures of the associations are seldom identified, they are generally believed to be chelates. Of the heavy metals required in plant nutrition, Cu is the one most strongly chelated by organic matter. McLaren and Craw-
ford extracted this fraction with $M \text{Na}_4\text{P}_2\text{O}_7$, and McLaren et al. with a mixture of $0.04M \text{Na}_3\text{PO}_4$ and $0.001M \text{Na-EDTA}$ at pH 7. Studying the soil solution, Hodgson et al. found that as much as 99% of the Cu present was chelated, but only about 40% of the Zn. Stevenson et al. observed that the formation constants for Cu binding to humic and fulvic acids were comparable to those observed for synthetic carboxylic acids. Lewis and Broadbent considered phenolic and carboxylic acids to be responsible. Davies et al. obtained a 50% reduction in retention of Cu by humic acid when carboxyl and hydroxyl groups were blocked. Khanna and Stevenson believed carbonyl groups to be responsible for retaining Cu and Zn in soil. Studying the bonding of Cu, Cd, and Pb by humic acids with specific ion electrodes, Bondietti and Sweeton found that the apparent stability constants were of the same general magnitude as those involving citric and oxalic acids, with the order $\text{Cu} > \text{Pb} > \text{Cd}$; small amounts of added metals were bound much more strongly than large amounts.

Matsuda and Ito observed that Zn retention in soils increased with humic and fulvic acid contents. Randhawa and Broadbent concluded that humic acid has at least three types of exchange sites capable of retaining $\text{Zn}^{2+}$, including carboxyl and phenolic acid groups. These authors also noted that 70% of Zn in their soils was retained by humic acid as $\text{Zn}^{2+}$ at pH 3.6, but as $\text{Zn(OH)}^{+}$ at pH 7.0. The stability constants of the resulting complexes were 4.4 and 6.8, respectively. Zinc was found to be chelated by several components of leaf sap, e.g., amino acids and ellagic acid. Some of these chelates can be leached from foliage by rain.

Using a specific ion electrode to determine stability constants involving humic acid, Cd was ranked third after Cu and Pb. At pH 7, Cd could be displaced from humic acid by Ni > Zn = Co > Sr. Like Cu, Cd was strongly bonded by fulvic acid. Whether in an organic (11.4% C), or an inorganic (0.6% C) soil, the toxicity of several heavy metals with regard to corn followed the order Cd > Cu > Pb.

In this paper, we present data on charged forms of Cd, Cu, and Zn in aqueous sewage sludge extracts, as influenced by pH. We used a resin technique, briefly introduced earlier to differentiate between cationic, anionic, amphoteric and neutral species, without regard to their molecular weight or valence. We examined the con-