

Metal-binding Role of Iron and Manganese Oxides in Biosolid-amended Soils

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Introduction

The environmental impact and potential hazards of metals in biosolids to plants, animals, and the human food chain have been studied for decades. From this body of work, it has been concluded that the addition of biosolids to the soil alters the soil system beyond that of the simple addition of greater quantities of trace elements [1]. Further, it is apparent that this alteration does not require large additions of biosolids. The phase or phases responsible for this alteration continue to be in dispute. Some researchers have postulated and supported the “time-bomb” hypothesis, in which it is assumed that the responsible phase is organic and that, as the organic material decomposes, its complexing nature gets lost, and it subsequently releases metal to the inorganic system, where it behaves as a salt addition to the soil [2]. In contrast, other researchers have predicted that biosolid adsorption chemistry is related to inorganic surfaces [3]. On the basis of these understandings, researchers began to characterize the chemical aspects of biosolids that made metals so much less available to plant systems (phytoavailable) or biological systems (bioavailable) than metal-salts. Studies from long-term field application sites illustrated that bioavailability does not increase as the added organic matter decreases.

Previous research from our laboratory with biosolids and biosolid-amended soils demonstrated that Cd sorption for biosolid-amended soils was intermediate to the control soil and that biosolids and increased with an increasing biosolid application rate. The removal of organic carbon reduced metal sorption but did not account for the observed differences between biosolid-amended soils and controls, indicating that the increased sorption associated with the application of biosolids was not limited to the increased organic carbon due to the addition of biosolids. Removal of Mn and/or Fe oxides reduced metal sorption in biosolid-amended soils, suggesting that the relative contribution of these inorganic fractions to metal sorption in biosolid-amended soils is significant [4]. Microscopic information that would provide an understanding of the reaction mechanisms and the reaction products of biosolids-metal interactions (in addition to the

macroscopic information) would provide greater confidence in the risk assessment conducted by the EPA.

Methods and Materials

Biosolids samples (Nu Erath) from Chicago, IL, were used in this experiment. Total concentrations of Zn, Cd, Pb, Cu, Mn, and Fe in dried biosolids were 4140, 210, 865, 1160, 302, and 25,000 mg/kg, respectively. An air-dried biosolids sample (crushed and sieved to #250 μm) was mounted in 5 \times 5-cm cardboard photographic slide mount by sandwiching several milligrams of the sample between two pieces of Kapton[®] tape that spanned the hole in the slide mount. Micro distributions of elements were obtained at a step size of 10 μm by using the x-ray fluorescence microprobe at GSECARS beamline station 13-ID-C.

Results and Discussion

The area of a single map shown in Fig. 1 is 220 \times 120 μm . In the color scheme employed, higher concentrations are light colors, with white indicating the most intense concentrations and blue/black indicating low concentrations. The curved feature in the map is an

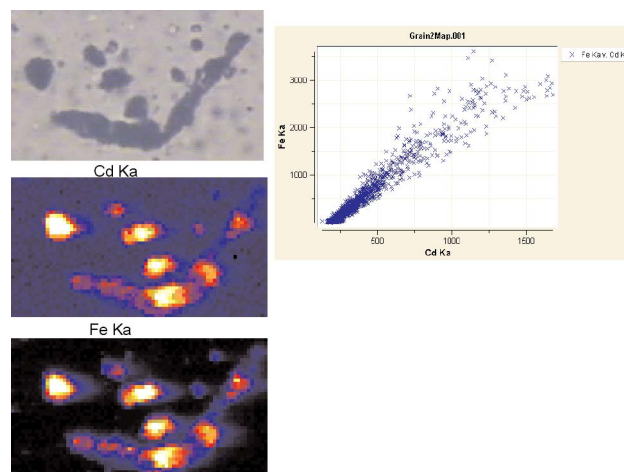


FIG. 1. Micro distribution of Cd and Fe for Nu Earth biosolids sample.

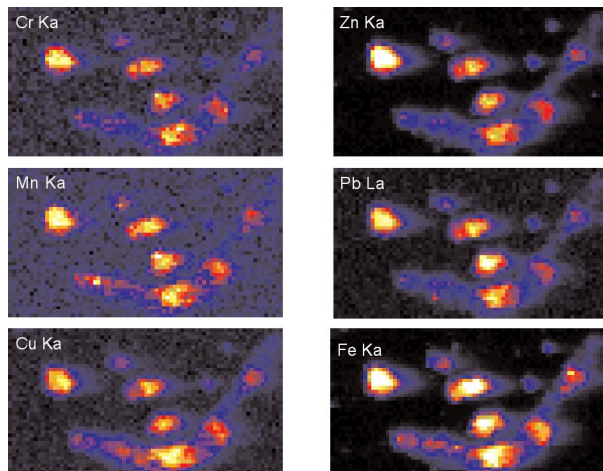


FIG. 2. Micro distribution of some selected elements (except Cd) and Fe for Nu Earth biosolids sample.

organic object coated heterogeneously with dark material. Iron and Cd distributions in the map area are shown in the lower left. Iron had several hotspots scattered on this organic object indicating that this dark-coated material could consist of Fe-rich compound(s). Although the Cd content was considerably lower than the Fe content, the distribution of Cd on this organic object was similar to that of Fe. Moreover, the correlation between Fe and Cd in this map area was constructed from x-ray fluorescence (XRF) data. The correlation between Fe and Cd was strong and positive. The correlation between Mn and Cd was not tested, because this biosolids sample does not contain Mn levels high enough to assume that Mn can control the Cd in this sample.

Distributions for other elements (Cr, Mn, Zn, Pb, and Cu) were also obtained from the same area in Fig. 1 as that shown in Fig. 2. All the other elements focused on in this study (Zn, Pb, Cr, Cu, and Mn) showed distinct

enrichments that correlate strongly with the enrichment zones of Fe in the map area. These observations were further proven true by the elemental correlations constructed from XRF data (data not shown). These microscopic observations support macroscopic observations (both laboratory and field) and indicate that Fe plays an important role in metal retention in biosolid samples. Retention could be due to the coprecipitation of these elements with Fe, the adsorption of these elements onto Fe, or a combination of both of these mechanisms.

Acknowledgments

This work was performed at the GSECARS sector 13 beamline at the APS. GSECARS is supported by the National Science Foundation (Earth Sciences), U.S. Department of Energy (DOE; Geosciences), W.M. Keck Foundation, and U.S. Department of Agriculture. Use of the APS was supported by the DOE Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

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