

X-ray Microscopy and Spectroscopy Studies on Metal Binding in Biosolids

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Introduction

Previous researchers have observed that metals added to soils as a constituent of biosolids are less phytoavailable than are metal salts added to soils with biosolids. Furthermore, they found that metal salts added to soils with biosolids are less phytoavailable than are metal salts added to soils without biosolids. These observations indicate that some phase(s) in biosolids keep metals unavailable for plant uptake. Those long-term experimental studies for which it is reported that the organic matter added by biosolids has equilibrated to background soil organic matter content illustrate that changes in the chemistry and phytoavailability of metals caused by biosolids application are unaltered by the decomposition of the added organic matter [1, 2]. Thus, it is implied that inorganic and/or very recalcitrant organic phases are responsible for the biosolid-induced reductions in metal phytoavailability.

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 biosolids and that it increased with an increasing biosolids application rate. 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 biosolids application 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 on metal sorption in biosolid-amended soils is significant.

In addition to macroscopic information, microscopic information that would allow an understanding of the reaction “mechanisms” and reaction products of biosolid-metal interactions would result in greater confidence in the risk assessments conducted by the U.S. Environmental Protection Agency.

Methods and Materials

Intact and organic-matter-(OM)-removed (treated three times with 0.7 M NaOCl adjusted to a pH of 8.5 at 90°C) limed composted biosolids (crushed and sieved to

$\leq 250 \mu\text{m}$) from the Blue Plains treatment plants in Washington, DC, were used in this experiment. Total concentrations of Zn, Cd, Pb, Cu, Mn, and Fe in dried biosolids were 731, 7.2, 272, 274, 719, and 41,000 mg/kg, respectively. Manganese and Fe oxidation state standards and semi-dry biosolid samples were mounted in $5 \times 5\text{-cm}$ cardboard photographic slide mounts 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 $10 \mu\text{m}$ by using the x-ray fluorescence microprobe on GSECARS beamline 13-ID-C. Since the biosolid sample had a comparatively higher level of Fe, elemental mapping was performed twice, at 14,000 and 7102 eV, to obtain Mn and Cr maps without interference from background Fe fluorescence. The $\mu\text{-XANES}$ (micrometer x-ray absorption near-edge structure) spectra of Fe and Mn were collected in fluorescence mode from seven to eight different randomly chosen “hot spots” of Fe and Mn from the elemental maps. In addition, $\mu\text{-XANES}$ spectra of Cr (at several hot spots of Fe and Mn in biosolid samples) and Mn and Fe standards were also collected.

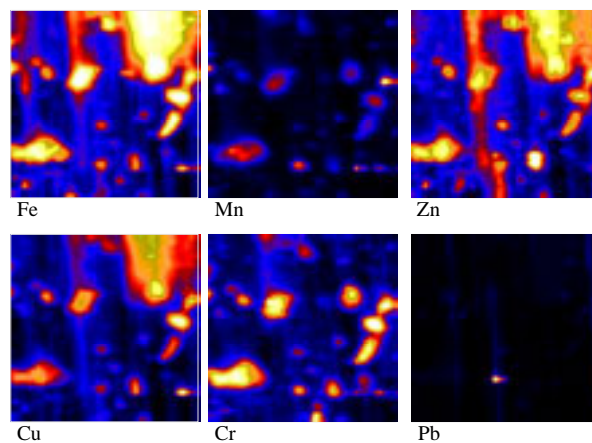


FIG. 1. Micro distribution of different elements for the intact limed composted biosolid sample. The area of a single map shown here is $400 \mu\text{m}^2$.

Results and Discussion

In the color scheme employed in Fig. 1, higher concentrations are light colors, with white representing the most intense concentrations and blue/black representing low concentrations. The biosolid materials mapped consisted of dispersed particles. This could be the reason that some regions in the map show an approximately zero concentration of all the elements mapped. Iron had several hot spots scattered in this 400- μm square. Although the Mn content was considerably lower than the Fe content, the distribution of Mn was similar to that of Fe. Three (Zn, Cu, and Cr) of the four other elements investigated in this study showed distinct enrichments in the biosolid sample that correlated with the enrichment zones of Fe and Mn. These observations were proved further by the elemental correlations constructed from x-ray fluorescence (XRF) data.

Correlations between Fe and Mn in both the intact and OM-removed samples were strong and positive, with r^2 values ranging from 0.8 to 0.78 (data not shown). Strong positive correlations were also observed between Cu, Zn, and Cr with Fe in the intact sample (Fig. 2). The observed lack of correlation between Pb and Fe was possibly caused by the poor distribution of Pb in the area chosen for mapping (Figs. 1 and 2). All the elemental correlations except Fe and Cu remained strong even after OM was removed, indicating that these elements are in direct association with Fe. The disappearance of the Fe/Cu relationship after removal of OM suggests that Cu was possibly associated with OM coatings that may have been present on Fe compounds. Elemental correlations with Mn, except Fe/Mn and Mn/Cr (always strong), were

improved after OM was removed from the system, indicating that OM-removal treatment has had some effects on Mn compounds. The majority of Mn hot spots in the OM-removed biosolid sample had a mix of 4+ and 2+ oxidation states, with 4+ being dominant over 2+, whereas those in the intact sample had the same mix of oxidation states, with 2+ being dominant over 4+. These microscopic observations support macroscopic observations (both laboratory and field) and indicate that Fe and Mn play an important role in metal retention in biosolid samples. This could be due to coprecipitation of these elements with Fe and/or Mn, adsorption of these elements onto Fe and/or Mn compounds, or a combination of both of those mechanisms.

Acknowledgments

This work was performed at GSECARS sector 13 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.

References

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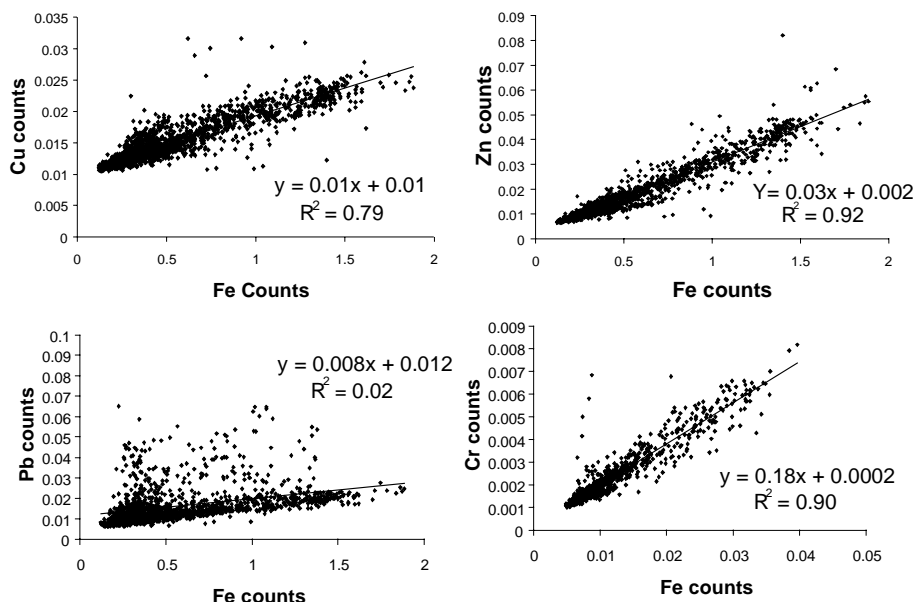


FIG. 2. Elemental correlations with Fe in the intact limed composted biosolid sample.