

Cd Speciation Associated with Iron Oxides and Biosolids

¹K. Scheckel, ²G. Hettiarachchi, ¹J. Ryan

¹United States Environmental Protection Agency, Cincinnati, OH, U.S.A.; ²University of Adelaide, Adelaide, SA, Australia.

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 the addition of biosolids to the soil alters the chemical phases in the soil system beyond that of the simple addition of greater quantities of trace elements. Further, it is apparent that this alteration does not require large additions of biosolids. The phase responsible for this alteration has and continues to be in dispute. In its development of regulations designed to protect human health and the environment from reasonably anticipated adverse effects of land application of biosolids, the U.S. Environmental Protection Agency's reliance on this difference in phytoavailability of metals in soil systems amended with biosolids, intensified the debate. Beckett et al. (1) postulated the "time-bomb" hypothesis in which it is assumed that the responsible phase is organic and as the organic material decomposes its complexing nature will be lost with a subsequent release of metal to the inorganic system where it will behave as a salt addition to the soil. In contrast, Corey et al. (2) predicted that biosolids adsorption chemistry related to inorganic surfaces control the activity in the soil after reaching saturated of soil metal binding sites. Based on these understandings, researchers began attempting to characterize the chemical aspects of biosolids, which made metals so much less available to plants (phytoavailable) or biological systems (bioavailability) than were metal-salts. Studies from long-term application sites illustrated that bioavailability does not increase as the added organic matter decreases.

Metals (such as Fe, Mn, and Al) are generally high in biosolids. Surfaces of freshly precipitated metal oxides, especially Fe and Mn, are known to be highly active sites for most dissolved metal ion species. We have previously conducted metal sorption/desorption studies which illustrate the importance of iron and manganese fractions in biosolids-amended soils to toxic trace metal retention. It is apparent that resolution of this issue can be accomplished by identification of the forms of metals and metal sorbents in soil systems accompanied with an understanding its persistence. In addition, speciation will provide information on metal mobility and therefore, other potential environmental problems such as ground water contamination. Direct observation of chemistry of metals in biosolids has not been successful so far because of the great complexity of sludge mineral and chemical forms (3), lack of crystallinity and smaller quantities (4).

In this work we investigated the distribution and speciation of metals in whole biosolids material via μ -XANES and μ -XRF.

Methods and Materials

The distribution and speciation of metals in biosolids were analyzed by μ -XRF mapping and μ -XANES. Metal μ -XANES spectra and μ -XRF maps were collected at beamline Sector 13-ID (GeoSoilEnviro Consortium for Advanced Radiation Sources (GSECARS)) at the Advanced Photon Source at Argonne National Laboratory, Argonne, IL. Energy calibration was accomplished by assigning the first inflection point of Ag foil to 25 514 eV. The electron storage ring operated at 7 GeV with a top-up fill status. Scans were collected at ambient temperature in fluorescence mode with a solid-state 13-element detector. The μ -XRF mapping employed a 6 μ m diameter spot size with a one second integration time per x-y step. Bulk XANES data were collected in fluorescence mode for reference standards and some biosolids analyses. XANES data were analyzed using WinXAS (5). The collected scans for a particular sample were checked for calibration, averaged, normalized, and the background was removed by spline fitting.

Results and Discussion

Figure 1 shows the XRF elemental maps of Fe, Cd, and other metals for the intact Nu Earth biosolids sample demonstrating the distribution and concentration relative to individual particles seen in the optical image in the upper left corner of each figure. The XRF maps visually show that "hotspots" of Fe (concentration gradient of white to black represents high to low count values) match well to similar distribution hotspots for the other various metals. In the Cd XRF map for Figure 1, two markers noted at "1" and "2" represent locations for which μ -XANES analysis was conducted with the XANES spectra presented in Figure 2.

These XANES spectra in Figure 2, which include bulk analysis of the Nu Earth biosolids, show Cd in the Cd⁺² oxidation state based on the position of the white line peak. The spectra for the Nu Earth intact samples (bulk and micro) are essentially identical indicating that Cd speciation is uniform in the biosolids. The Cd XANES spectra of goethite with adsorbed Cd and coprecipitated Cd show a distinction in the sorption mechanism. The Cd XANES spectra for adsorbed Cd show a distinctively sharp, narrow white line peak whereas the XANES spectra for coprecipitated Cd exhibit a shorter and broader white line peak compared to the adsorbed spectra.

By comparing the differences in adsorption and coprecipitation of Cd with Fe-oxides, one observes nearly identical XANES spectra for adsorbed Cd and Cd in the Nu Earth biosolids samples with no noticeable influence of Cd coprecipitation. The results show that Cd and other trace metals are directly associated with inorganic Fe phases and XANES analyses show that Cd is present as an adsorbed species to an Fe oxide phase.

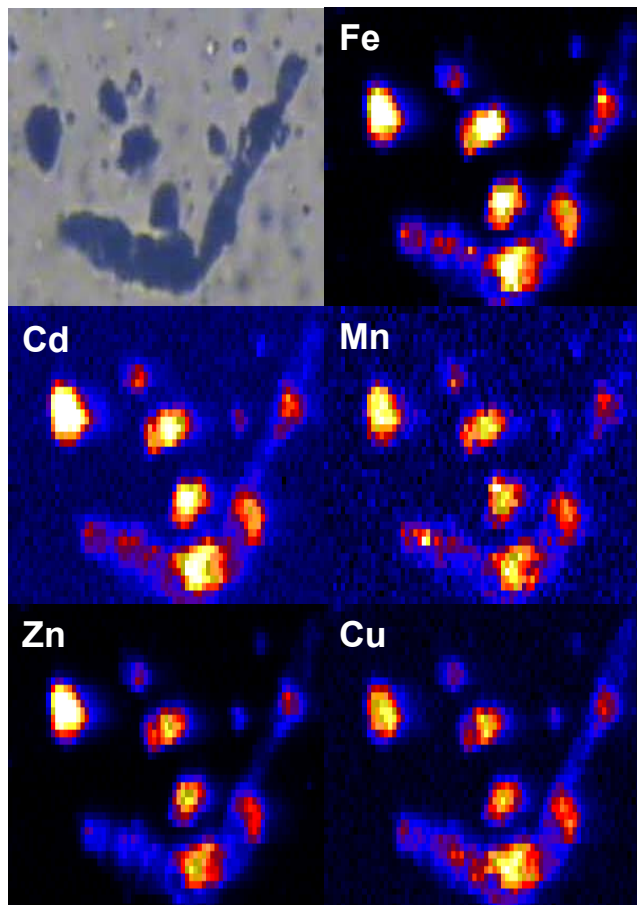


Figure 1. X-ray fluorescence maps of metals in Nu Earth biosolids.

Discussion

Microscopic observations made in this study support macroscopic observations (both laboratory and field) indicating that Fe (and possibly Mn) play an important role in metal retention in biosolids 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 combination of both of those mechanisms. Our studies suggest that the “time-bomb” theory by Beckett et al. (1) is not well founded. Further, this study also shows that the employment of synchrotron-based research methods to examine biosolids and complex environmental samples is possible and these techniques will greatly enhance our understanding of such systems.

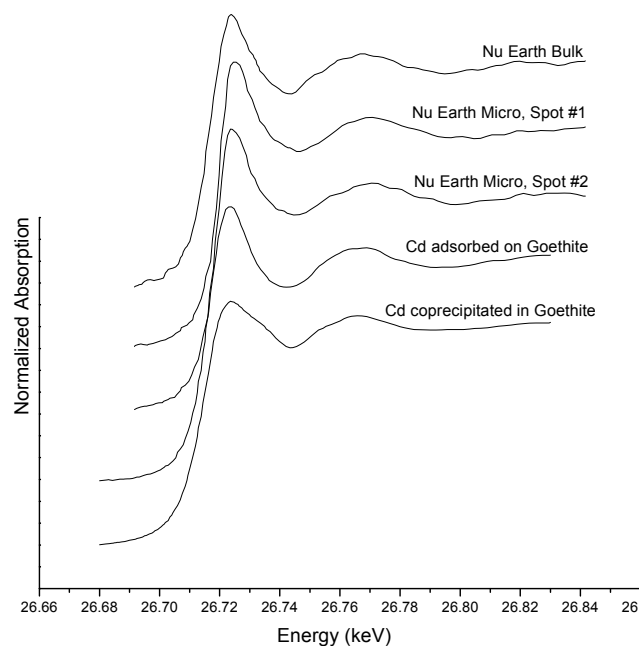


Figure 2. X-ray absorption near-edge (XANES) spectra of Nu Earth biosolids and Cd sorption references.

Acknowledgments

We thank the beamline staff at Sector 13 (GSECARS) for their generous assistance with this project. Use of the Advanced Photon Source was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. W-31-109-ENG-38.

References

- (1) Beckett, P. H. T.; Davis, R. D.; Brindley, P., The disposal of sewage sludge onto farmland: The scope of the problems of toxic elements. *Water Pollut. Control* **1979**, *78*, 419-445.
- (2) Corey, R. B.; King, L. D.; Leu-Hing, C.; Fanning, D. C.; Street, J. J.; Walker, J. M. Effects of sludge properties on accumulation of trace elements by crops. In *Land application of sludge*; al., A. L. P. e., Ed.; Lewis Publishers: Chelsea, MI, 1987; pp 25-51.
- (3) Lake, D. L.; Kirk, P. W. W.; Lester, J. N., Fractionation, characterization, and speciation of heavy metals in sewage sludge and sludge-amended soils: A review. *J. Environ. Qual.* **1984**, *13*, 175-183.
- (4) Essington, M. E.; Mattigod, S. V., Trace element solid-phase association in sewage sludge and sludge-amended soil. *Soil Sci Soc Am J* **1991**, *55*, 350-356.
- (5) Ressler, T., WinXAS: A program for X-ray absorption spectroscopy data analysis under MS-Windows. *J. Synchrotron Rad.* **1998**, *5*, 118-122.