Nanoparticles in biosolid products as revealed by electron microcopy

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The production and use of engineered nanoparticles has been rapidly increasing for the past few years. As of 2009, the Project on Emerging Nanotechnologies at the Woodrow Wilson International Center for Scholars had made an inventory of more than 1, 000 consumer products that claim to have some forms of engineered nanoparticles. Engineered nanoparticles in consumer products are expected to be released into wastewater streams to a degree during and/or after the lifetime of the products, which in turn may raise concerns about their potentially adverse impact on the environment.

Biosolid materials are the byproducts of processes that clean our wastewater before the cleaned water is discharged into the aquatic environment. During these proceeses, nanoparticles may be incorporated into the biosolid matrix through aggregation and/or sorption reactions. Because nanoparticles concentrated in the biosolids may be redistributed into other environmental components, for example, through land application, incinertation or landfilling, it is very important to investigate the nature of nanoparticles in biosolid materials to assess their potential risk.

In the present study, we employed transmission electron microscopy (TEM) and scanning TEM (STEM) combined with energy dispersive X-ray specroscopy (EDX) for direct visulaization and characterization of nanoparticles in biosolid samples with sub-nanometer resolution. We successfully identified nano-sized Si and Al oxides, Ti oxides, and Ag and Zn nanoparticles in the biosolid samples with detailed analyses including the size, morphology, elemental compositions, and degree of crystallinity and aggregation. The results of our work clearly show the presence of nanoparticles in biosolid products with a great degree of heterogenity and complexity. This study will help us to evaluate further risks when these biosolid products reenter the environment.

(Micro)spectroscopic investigations of arsenic speciation trends in mine wastes

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Extensive gold and silver mining has left a legacy of contaminated mine wastes across the state of California, where large volumes of mine tailings and waste rock contain highly elevated concentrations of naturally-occurring arsenic. Characterizing trends in arsenic speciation as a function of particle size can provide insight into the processes that control arsenic transport from mine-impacted sites.

Bulk mine waste samples from the Randsburg Historic Mining District in Southern California were collected and weighed prior to dry sieving to generate 11 size range-specific fractions (from >2830 um down to <20 um). Each fraction was weighed and analyzed using ICP-AES for concentrations of 48 separate elements including arsenic, iron, and other potentially toxic metals. Micro- and bulk spectroscopic methods were then applied to selected size fractions of mine wastes, utilizing X-ray fluorescence and X-ray absorption spectroscopy (XAS) to assess the speciation, distribution, and correlation of metals of interest. Finally, the availability of arsenic from mine wastes through exposure to water or passive ingestion or inhalation was examined by leach extractions using water, a simulated gastric fluid (SGF), and a simulated lung fluid (SLF), with spectroscopic studies conducted on selected samples before and after the extractions to assess potential changes in speciation.

Results show that arsenic is typically more concentrated in the finer grain size fractions, often by over an order of magnitude, potentially increasing its mobility, reactivity, and bioavailability. A mixture of arsenic-bearing species were identified by micro- and bulk XAS in most size fractions, including the presence of phases including scorodite ($FeAsO_4$), arseniosiderite (Ca_2Fe_3 [O_2 $(AsO_4)_3$]•$3H_2O$), and As (V) sorbed to ferrihydrite. Slight changes in arsenic speciation with particle size correspond to the removal of more soluble crystalline phases and the formation of sorbed arsenic species (i.e. to iron oxyhydroxides), which may partially offset the potential toxicity of arsenic in fine-grained fractions. However, SGF studies show that under acidic conditions arsenic is still preferentially released in the finer fractions, even when corrected for surface area effects, and that more soluble arsenic phases can be shown to be preferentially removed during SGF extractions.