Engineering at the Interface: Integrating Laboratory Research and Modeling to Assess Nanosilver Risk

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Introduction

The global market for nanotechnology is estimated to have reached $15.7 billion in 2010 and is expected to grow to approximately $26.7 billion by 2015. Nanosilver, which is used as an additive in many products (e.g., plastics, textiles) because of its antibacterial properties, is the most widely advertised nanomaterial in consumer goods. Understanding the fate and transport of nanosilver is environmentally important because nanosilver and the silver ion released during dissolution are known to be toxic to a wide range of aquatic invertebrates, fish, and estuarine organisms.

Our goal with this project is to develop a model describing the physical and chemical transformations nanosilver undergoes once released to the environment. These fate and transport processes are highly complex (Figure 1) and therefore present the perfect opportunity for cross-disciplinary work. Our research integrates laboratory research and field studies on the behavior of nanosilver and transformed silver species in the environment with a computational/mathematical approach to modeling and risk forecasting.

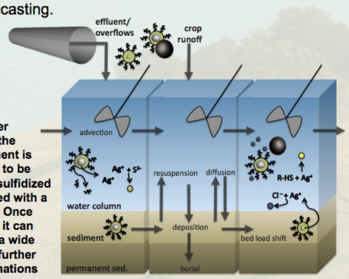
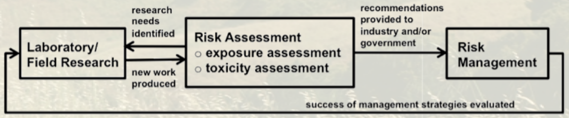


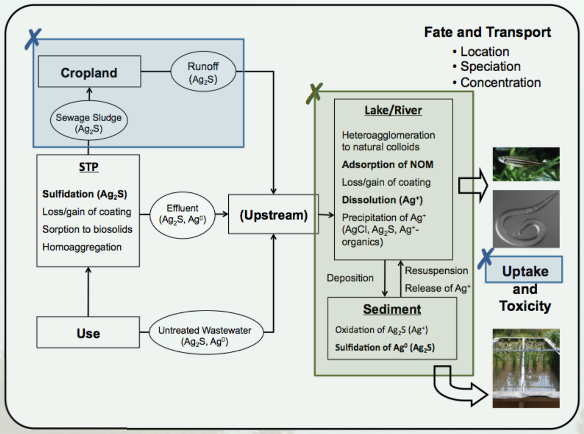
Figure 1. Nanosilver entering the environment is expected to be partially sulfidized and coated with a polymer. Once released, it can undergo a wide range of further transformations

Our preliminary work highlights the value of developing the model as part of a larger risk assessment framework. This will allow us to develop optimal management strategies that maximize the benefits of nanosilver while minimizing their environmental impact (Figure 2).

Figure 2 (below). Diagram detailing relationships between laboratory and field research, risk assessment, and risk management. By integrating laboratory and field research with mathematical and computational assessments of exposure and toxicity, we maximize the efficiency of these relationships.



Model Framework



✗ Speciation in Freshwater and Sediment

Figure 3. The CEINT mesocosms are large batch reactors exposed to the environment. They have sloped soil beds and are half-filled with water. They are stocked with fish and both an aquatic and a terrestrial species of plant.

The interuniversity research consortium CEINT (Center for Environmental Implications of Nanotechnology) created mesocosms (left) to study the fate and transport of nanosilver in an artificial freshwater wetland. The mesocosms were spiked with nanosilver and sampled over 18 months. We characterized these samples and discovered almost all of the metallic silver (Ag^0) had quickly settled out of the water column into the sediment and much had converted to silver sulfide (Ag_2S).

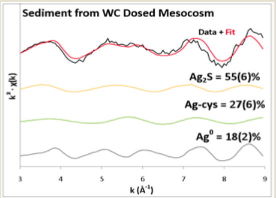
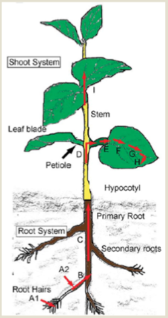


Figure 4. LCF analysis showing Ag_2S dominates silver speciation in the sediment 18 months after exposure

✗ Biouptake in Plants/Speciation in Crop Soils

Figure 5. Routes of uptake, transport, and accumulation of nanoparticles in plants. A2: absorption by primary roots. A1 → B: absorption by lateral roots. Particles are then transported from the root to the stem and leaf (C →D, I → E-H).

From Ma, X., J. Geiser-Lee, et al. (2010). "Interactions between engineered nanoparticles (ENPs) and plants: Phytotoxicity, uptake and accumulation." <u>Science of the Total Environment</u> 408(16): 3053-3061



We have recently begun to characterize nanosilver and silver sulfide uptake in plants. Our goal is to track speciation of the silver as it migrates throughout the plant (left). We intend to determine the rate law governing metal and metal sulfide uptake and transport. These experiments will be valuable in determining the long-term fate of nanosilver in agricultural soils. This, in turn, will determine the nature of silver inputs to surface waters resulting from runoff during heavy rains.

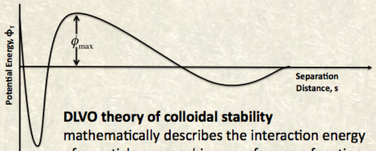
Learning from re-oxidation of zinc sulfide

Both silver sulfide and zinc sulfide re-oxidize in activated sewage sludge to form metal sulfates or metal phosphates. We are currently developing batch experiments to study this process, which could impact heavy metal accumulation and phytotoxicity in agricultural crops grown in sludge-amended soils. By learning more about the transformations common to silver, zinc, and other class B metals (right), we can more efficiently determine and manage the risks associated with the nanoparticulate form of these metals.

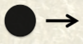
Some class B (soft) metals

- ✗ **Silver**
- ✗ **Zinc**
- ✗ Gold
- ✗ Palladium
- ✗ Lead
- ✗ Platinum
- ✗ Mercury
- ✗ Rhodium

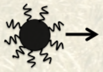
Modeling Nanosilver Fate and Transport



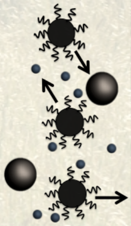
DLVO theory of colloidal stability mathematically describes the interaction energy of a particle approaching a surface as a function of its distance from the surface



Classic DLVO describes an uncoated particle approaching a surface

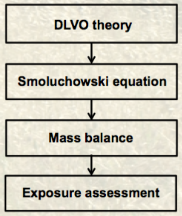


Extended DLVO describes a particle with a coating approaching a surface



The **Smoluchowski equation** describes the frequency and success of collisions between particles and surfaces as a function of Φ_{max} (left)

Mass balance provides a mathematical framework with which to describe transport processes (e.g., advection, settling) and transformation processes (e.g., dissolution) affecting the total mass of a substance in the environment



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