Gold Nanoparticle Biodissolution by a Freshwater Macrophyte and Its Associated Microbiome

Natural and engineered nanomaterials are particles with one dimension <100nm. They can have unique reactivity compared to larger particles with the same chemical composition. However, there is still limited understanding of how these nanophases will behave once released into complex natural ecosystems. The Center for Environmental Implication of NanoTechnology (CEINT) built a facility containing 30 large-scale freshwater wetland mesocosms to study the fate of engineered nanomaterials when added to natural freshwater emergent wetlands over long times at low dose. These ~3m^3 mesocosms undergo seasonal changes and contain all of the complexity of a real emergent freshwater wetland and are therefore great tools for understanding how nanomaterials will behave in real environments. The mesocosms contained:

- an upland zone, not flooded, containing soil and terrestrial plants
- a transition zone (soil on a slope) that is wet or dry depending on the water level and it contains juncus (plants)
- an aquatic zone filled with ~250L of water that contain sediment at its bottom, fish, clams, macroinvertebrates and aquatic plants.

Left: CEINT mesocosm facility. *Right:* Weekly dosing of Au NPs.

The initial goal of this study was to assess how a nanoparticle that dissolves will behave in comparison with a stable, inert one. Au NPs were chosen as a NP tracer because, according to the literature and conventional wisdom, they were "inert" and could trace how NPs move around between different environmental compartments. In this particular study, about 75mg of Au NPs were added each week for 6 months. This is equivalent to about 70 parts-per-billion in the water column. The research team used a long-term low concentration input of Au NPs to best mimic how they might be introduced into the environment, e.g. in low doses in wastewater treatment. To measure Au NP fate, sediment, soil, plants, and organisms were measured every three months. The team also monitored the environmental conditions daily or weekly to fully characterize the system (for instance light, temperature pH, oxygen, carbon dioxide). For the compartments accumulating the most Au (plants in this case), the researchers measured the speciation of the gold using synchrotron x-ray absorption spectroscopy at SSRL on Beam Line 11-2. This work could not have been done without access to SSRL.

After three months, the research team realized that the aquatic plants accumulated very high concentrations of Au (the majority of the Au added into the system). When used XAS was used to measure gold speciation in the aquatic plants, the researchers realized that all of the Au NPs were oxidized and transformed Au species that were not metallic, its initial speciation. This was surprising finding because Au is known to be stable against oxidative dissolution in oxic waters, and thus had been used as a tracer for nanoparticles in more than 20 prior studies.

The research team then set out to determine the mechanisms responsible for dissolving the Au NPs. They hypothesized it had to be a biologically driven mechanism. The microorganisms living on the aquatic plant surface (called biofilm) were extracted. The team characterized the type of microorganisms present, their capacity to dissolve Au NPs, and then correlated this with their ability to release cyanide (which is a molecule known to dissolve and complex Au). Before this study, no one had demonstrated that Au NPs could dissolve in freshwater aquatic environments. In fact, the opposite was dogma. Cyanide is a very strong complexing agent, and similar biotransformation are likely to occur with other metallic nanoparticles as well. This study also points to biofilms of freshwater plants as an interesting environmental compartment to study to better understand its role in the biogeochemical cycling of engineered nanomaterials, and in metals in general.

The conditions that promote the biodissolution of engineered nanomaterials (transformation from a solid state to an ionic state) is needed to accurately predict the fate and effects of nanoparticles. Biodissolution can lead to different routes and rates of transport and bioaccumulation, different toxicity, and different rates of transfer into the food chain compared to the nanoparticulate form. These findings suggest that the assumption of Au NP stability may not be a good one. More than 20 papers have been published using Au NPs as “particle tracers”. Resulting conclusions about bioavailability and toxicity based on the assumption that the Au NPs had not dissolved may need to be revisited. This study demonstrates that biotransformation are happening in complex environments, even for nanoparticles that are thermodynamically stable in water without organisms, and that these transformations can happen very quickly.

A next step for the researchers is to leverage this new understanding about the role of plant biofilms on nanomaterial fate towards designing better nano-enabled products, e.g. agrochemicals. Perhaps the phytobiome can be used to deliver agrochemicals (e.g. micronutrients like Fe or Cu) better. The team would also like to better understand how these biofilms affect the fate of other nanomaterials in the environment. Finally, there are still many unanswered questions about how environmental complexity influences nanomaterial fate and impacts. Future mesocosm experiments will help to elucidate the fate processes of engineered nanomaterials in the environment.

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