Experimental transformations of zinc oxide nanoparticles in redox-dynamic freshwater sediments

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The increasing release of ZnO nanoparticles from anthropogenic sources raises concern regarding their fate in the environment, especially since soils and sediments are found favorable for their accumulation [1]. Whereas studies on unsaturated soils showed that, ZnO is converted into Zn-rich layered double hydroxides and Zn adsorbed species, in the presence of sulfides, it is recognized that ZnO transform into ZnS phases [2,3]. However, despite formation of ZnS has been reported in environmental samples [4], the fate of ZnO nanoparticles in redox-dynamic sediments is still poorly understood. Here, based on laboratory experiments, we investigated the fate of ZnO nanoparticles in sediments and assessed the geochemical and physicochemical factors controlling ZnO nanoparticles transformation.

Lacustrine sediments were spiked with ZnO nanoparticles and incubated under either oxic or anoxic conditions. Using EXAFS spectroscopy at the Zn K-edge and geochemical analyses, we revealed the rapid dissolution of ZnO nanoparticles under oxic conditions within a few hours. Zn released from dissolving ZnO nanoparticles mainly adsorbs onto phyllosilicate minerals. By contrast, ZnO nanoparticles dissolution under anoxic conditions is much slower, with $\sim 20\%$ of ZnO nanoparticles remaining after 81 days of incubation. Only 40% of the total Zn is found in the form of amorphous ZnS, in mixture with Zn adsorbed species. In contrast, ZnS is the only observed specie in the control experiments spiked with dissolved Zn²⁺. While under oxic conditions, the presence of intermediate Zn-organic species suggest that ZnO nanoparticles dissolution is enhanced by organic compounds, EXAFS spectroscopy combined with geochemical analyses suggest that ZnO dissolution, the formation of free Zn²⁺ and the adsorption to sediment particles under anoxic conditions is inhibited by the presence of sulfides.

Altogether, our results bring important information on the stability of ZnO nanoparticles in redox-dynamic sediments and show that further investigations are needed to better understand the mechanisms controlling ZnO nanoparticles fate in such environments.

[1] Gottschalk et al. *Environmental Pollution* **2013**, 181, 287-300

[2] Voegelin et al. *Environmental Science & Technology* **2011**, 45, 255–261

[3] Ma et al. *Environmental Science & Technology* **2013**, 47 (6), 2527–2534