

Natural nanoparticles: Formation and impact on trace elements

ANDREAS VOEGELIN

Eawag, Swiss Federal Institute of Aquatic Science and Technology, Switzerland (andreas.voegelin@eawag.ch)

Natural nanoparticles profoundly impact the fate of trace elements in terrestrial and aquatic systems as catalysts, immobilizing sorbents or colloidal carriers. Two systems will be discussed in which redox-processes induce the high degree of supersaturation that leads to nanoparticle precipitation.

(i) Flooding of contaminated wetland soils may lead to the release of trace metals into aquatic systems. In microcosm experiments, we found substantial mobilization of colloidal Cu, Hg, Pb and Cd into porewater upon soil flooding [1,2]. Spectroscopic and microscopic evidence (XAS and TEM) showed that this was initially due to bacterially-mediated formation of Hg-containing Cu(0) nanoparticles. Microbial sulfate reduction subsequently led to Cu(0) sulfidation and the formation of new Cu-rich metal sulfide nanoparticles that also contained Cd, Pb and Hg. These findings demonstrate that formation of metallic and metal sulfide nanoparticles may mobilize metals into soil porewater. Their importance for long-range metal transport however will depend on additional factors including their colloidal mobility in the subsurface and oxidative dissolution kinetics in oxic water bodies.

(ii) The oxidation of Fe(II) by O₂ at anoxic/oxic boundaries induces the precipitation of nanoparticulate Fe(III)-precipitates with a high capacity for cation and anion uptake. Related to studies on As removal from anoxic Fe(II)-containing groundwater in Asia, we studied how phosphate, silicate and Ca affect the formation, structure and As uptake of Fe(III)-precipitates [3-5]. XAS and TEM analyses showed that the structure of precipitates formed over a wide range of conditions systematically varied between several end-members, most importantly lepidocrocite, ferrihydrite and amorphous Fe(III)-phosphate. These results provide the basis for a better understanding of the link between water chemistry and the formation of different Fe(III)-precipitates with different chemical and colloidal reactivity. Such knowledge is essential for assessing the impact of Fe(III)-precipitates on nutrient and trace element cycling in the environment and their optimal use in engineered systems for water treatment.

[1] Weber *et al Nature Geosci.* **2**: 267, 2009 [2] Hofacker *et al Environ. Sci. Technol.* **47**: 7739, 2013 [3] Voegelin *et al Geochim. Cosmochim. Acta* **74**: 164, 2010 [4] Kaegi *et al Geochim. Cosmochim. Acta* **74**: 5798, 2010 [5] Voegelin *et al Geochim. Cosmochim. Acta* **117**: 216, 2013