

Effect of NOM on copper sulfide nanoparticle growth and stability

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Trace metals can be enriched in natural environments either naturally or through anthropogenic activities. In redox-dynamic environments that are subject to periods of prolonged waterlogging (river floodplains, wetlands), available sulfate is microbially reduced and nanoscale precipitates of sparingly soluble metal sulfides form (e.g., Cu_xS, CdS). These nanoparticles may dissolve upon re-establishment of oxic conditions. The relevance of NOM as key factor affecting particle growth and stability has been shown for other metal sulfides, e.g., HgS [1]. But up to now, knowledge of NOM effects on Cu_xS growth and dissolution behavior is lacking.

In this study, we performed experiments on Cu_xS nanoparticle formation in anoxic aqueous solutions with varying metal (50, 500 μM) and sulfide (100, 1000 μM) concentrations in the absence and presence of Suwannee River Fulvic Acid (0, 5, 50 mg C/L). The growth of Cu_xS nanoparticles was tracked by size-exclusion chromatography (SEC) coupled with ICP-MS and transmission electron microscopy (TEM) over the course of four weeks. Additional dissolution experiments were conducted in closed containers in the absence and presence of O₂ and fulvic acid over several months.

Our results highlight the extraordinary colloidal stability of Cu_xS nanoparticles in anoxic environments regardless of the NOM concentration. Median particle sizes, that ranged between 2 – 45 nm, were strongly dependent on absolute reactant concentrations. In low concentration experiments, metal sulfide clusters < 1 nm were detected. Fulvic acid restricted particle growth, which was reflected in significantly smaller particle sizes after four weeks. Oxidative dissolution of Cu_xS particles only took place when fulvic acid was present. Our results suggest an increased mobility of the copper sulfide nanoparticles in NOM-rich environments, but also point to enhanced oxidation of Cu_xS and release of Cu²⁺ ions in the presence of NOM upon aeration of anoxic waters.

[1] Deonarine, A. and Hsu-Kim, H. (2009) *Environ. Sci. Technol.* **43**, 2368-2373.