

Phosphate co-precipitation with Fe(III) during Fe(II) oxidation: Effects of dissolved organic compounds

VILLE NENONEN^{1,2}, RALF KAEGI¹, STEPHAN J. HUG¹, STEFAN MANGOLD³, JÖRG GÖTTLICHER³, LENNY H.E. WINKEL^{1,2} AND ANDREAS VOEGELIN¹

¹Eawag, Swiss Federal Institute of Aquatic Science and Technology

²ETH, Swiss Federal Institute of Technology, Zurich

³Karlsruhe Institute of Technology

Presenting Author: ville.nenonen@eawag.ch

The oxidation of dissolved Fe(II) in natural waters leads to the precipitation of amorphous to poorly-crystalline Fe(III)-solids that can sequester dissolved phosphate (PO₄). Dissolved organic matter (DOM) may affect the structure, colloidal mobility, and PO₄ binding of the Fe(III)-precipitates. However, to date, mechanistic studies on the effects of DOM on the formation, properties, and PO₄ uptake of Fe(III)-precipitates formed by Fe(II) oxidation in natural waters in the presence of other solutes (Ca, PO₄) are still scarce.

We studied the effects of organic ligands (citrate, 2,4-dihydroxybenzoate, 3,4-dihydroxybenzoate, galacturonate, humate) on the structure and colloidal stability of Fe oxidation products and on the co-precipitation of PO₄ and organic carbon (OC). Laboratory experiments were performed in bicarbonate-buffered (pH 7.0) aqueous solutions, with Na or Ca as electrolyte. Fe(III)-precipitate formation was initiated by spiking 0.5 mM Fe(II) to aerated solutions, at initial molar ratios PO₄/Fe of 0.05 or 0.25 and OC/Fe ratios of 0.1–9.6. Dissolved Fe, P, Ca, and organic C were measured in filtered samples. Fresh suspensions were analyzed for particle sizes and zeta potentials by dynamic and electrophoretic light scattering. The local coordination of Fe in the solids was probed by extended X-ray absorption fine structure spectroscopy, the bonding of Fe, PO₄, and OC by Fourier-transform infrared spectroscopy, and particle morphology and element distribution by scanning transmission electron microscopy with energy dispersive X-ray detection.

The Fe(III)-precipitates formed in the OC-free control experiments were mixtures of amorphous Fe(III)-phosphate and poorly-crystalline lepidocrocite. Increasing OC concentrations led to decreasing lepidocrocite crystallinity and to increased formation of ferrihydrite instead of lepidocrocite, resulting in more effective PO₄ and OC binding. Higher PO₄ concentrations resulted in decreased OC coprecipitation with Fe(III). Furthermore, higher OC concentrations resulted in smaller aggregate sizes and more negative zeta potentials, which increased colloidal stability of the precipitates. These effects decreased in the order citrate>3,4-dihydroxybenzoate>galacturonate>2,4-dihydroxybenzoate≥humate; with decreasing strength of Fe(III)-OC complexation.

In conclusion, the studied organic ligands can enhance co-precipitation of PO₄ with Fe(III) via their effect on the structure