

## Effect of citrate on the structure of ferrihydrite, arsenate binding, and ternary complex formation

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In oxic environments contaminated with arsenate (As(V)), polyhydroxycarboxylates such as citrate may impact the structure of precipitating ferrihydrite (Fh) and thus the surface speciation of As(V). In this study, 2-line Fh was precipitated from ferric nitrate solutions that were neutralized to pH 6.5 in the presence of increasing citrate concentrations and in the absence or presence of As(V). The initial citrate/Fe and As/Fe ratios were 0-50 mol% and 5 mol%, respectively. The reaction products were characterized by XRD, TEM and Fe and As K-edge XAS. Citrate decreased the particle size of Fh by impairing the polymerization of Fe(O,OH)<sub>6</sub> octahedra along and between dioctahedral chains, thus reducing the number of octahedral edge/face and corner linkages. In the presence of citrate and As(V), coordination numbers of second-shell Fe decreased by up to 25% relative to pure Fh. Citrate significantly reduced the distortion in Fe(O,OH)<sub>6</sub> octahedra of Fh, implying less surface strain. However, mean bond distances in Fh were not affected by citrate and remained constant within error at 1.98 Å for Fe-O, 3.03 Å for Fe-Fe1, and 3.43 Å for Fe-Fe2. Likewise, citrate had no effect on the As-Fe (3.32 Å) bond distance in As(V) coprecipitated with Fh. The As K-edge EXAFS data comply with the formation of a mixture of monodentate (<sup>1</sup>V) and bidentate binuclear (<sup>2</sup>C) As(V) surface complexes dominated by the latter. Our results suggest that increasing citrate concentrations led to a decreasing <sup>1</sup>V/<sup>2</sup>C ratio and/or that citrate decreased the static disorder in the As-Fe bond. Moreover, citrate electrostatically stabilized Fh in solutions of pH 4.3 - 6.6 and ionic strengths of ~0.45 M, and reduced Fh formation at the expense of soluble Fe(III)-citrate complexes. At initial citrate/Fe ratios ≥25 mol%, between 8% and 41% of total Fe was bound in Fe(III)-citrate complexes after Fh formation. While mono- and oligomeric Fe(III)-citrate complexes coexisted in the solutions, the oligomeric Fe(III)-citrate species were found to bind As(V) via formation of ternary As(V)-Fe(III)-citrate complexes. Our study implies that polyhydroxycarboxylates may enhance the mobility of As(V) in aqueous systems of high ionic strength (e.g. neutralizing acid mine drainage) by electrostatic stabilization of Fh particles and the formation of ternary As(V) complexes.

## Complexation and reactivity of mercury with natural organic matter (NOM) and particles in East Fork Poplar Creek in Oak Ridge, Tennessee, USA

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Kinetic controls on the complexation and reactivity of inorganic mercury (Hg) is often overlooked but may greatly influence the aquatic transformation and cycling of Hg. Using reducible Hg measurements on creek water and solutions containing dissolved natural organic matter (NOM) isolates, we found that the formation rate of Hg-NOM complexes ( $k = 0.05 - 0.29 \text{ hr}^{-1}$ ) are on time scales that are likely important in affecting the reactivity of Hg in the EFPC aquatic ecosystem. Competitive ligand titrations showed that the strength and reactivity of Hg-NOM complexes increases with increasing equilibration time between the Hg and NOM. This likely is a result of the transfer of Hg from weaker to strong binding sites within the macromolecular NOM structure. In the upper 2.5 km of EFPC, kinetic controls on Hg complexation is evident by the presence of reducible Hg at concentrations higher than expected if the complexation between Hg and NOM is instantaneous and equilibrium was established in the system. The interaction of Hg with particles is also kinetically controlled in EFPC with particulate bound Hg increasing downstream. Understanding the association of Hg with NOM and particles in EFPC is a critical step in elucidating the controls on Hg methylation and Hg redox cycling in this system.