Interactions between dissolved organic matter and mercury in aquatic environments

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Interactions of mercury (Hg) with dissolved organic matter (DOM) and aquatic humic substances play important roles in controlling the reactivity, bioavailability and transport of Hg in aquatic systems. Our research has shown that DOM influences the transport and reactivity of Hg by strong Hg-DOM binding and colloidal stabilization of mercuric sulfide (HgS) under all redox conditions. Strong interactions (K_{DOM}' = $10^{23.2\pm0.5}$ L kg^{-1} at pH = 7.0 and I = 0.1), indicative of Hg-thiol bonds, were observed at Hg/DOM ratios below approximately 1 µg Hg per mg DOM. Only a small fraction (approximately 2%) of the reduced-S groups, as determined by X-ray absorption near edge spectroscopy, was involved with these stronge interactions between Hg and DOM. These results suggest that the binding of Hg to DOM under natural conditions (low Hg/DOM ratios ranging from 0.01 to 10 ng of Hg/mg of DOM) is controlled by a small fraction of DOM molecules containing reactive thiol functional groups. In the case of fully oxygenated water (sulfide-free), the binding of Hg^{+2} by DOM should dominate dissolved inorganic mercury speciation. Where measurable total sulfide concentrations are present in surface water and pore water, Hg-sulfide complexes predominate. In these cases, which are common in sulfate reducing environments, DOM interacts strongly with HgS (log K_{sp} = -52.4) to inhibit aggregation and precipitation of HgS by colloidal stabilization. In experiments designed to define this interaction, precipitation of HgS was strongly inhibited in the presence of low concentrations (<3 mg C/L) of DOM, and organic matter rich in aromatic moieties was more reactive with HgS than less aromatic fractions. Aquatic humic substances were observed to inhibit the precipitation of HgS to a greater degree than low molecular weight ligands and other fractions of DOM. These results suggest that DOM can influence the geochemistry and bioavailability of HgS in aquatic environments by maintaining higher dissolved total Hg concentrations than predicted by speciation models.

The influence of dissolved organic matter on cinnabar dissolution

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Cinnabar (HgS) dissolution rates were measured in the presence of twelve different natural dissolved organic matter (DOM) isolates, including humic, fulvic, and hydrophobic acid fractions. Initial dissolution rates ranged over 1.3 orders of magnitude, from 2.31×10^{-13} to 7.16×10^{-12} mol Hg (mg C)$^{-1}$ m^{-2} s^{-1}, and produced dissolved Hg concentrations orders of magnitude above those expected in purely inorganic solutions. Rates were positively correlated with three characteristics of the DOM: specific ultraviolet absorbance at 280 nm (R^2 = 0.88), aromaticity (R^2 = 0.80), and molecular weight (R^2 = 0.76). Three observations demonstrate that direct interaction of DOM was necessary to cause dissolution of the cinnabar surface: (1) rates of Hg release were linear with time, (2) rates were significantly reduced when the DOM was physically separated from the surface by 1000 Dalton dialysis membranes, and (3) rates approached maximum constant values at a specific ratio of DOM concentration to cinnabar surface area, suggesting that rates are a function of surface coverage by dissolution-reactive DOM. Dissolution rates for the hydrophobic acid fractions correlate negatively with sorbed DOM concentrations, indicating the presence of a DOM component or components that reduced the surface area of cinnabar that can be dissolved. When two hydrophobic acid isolates that enhanced dissolution to different extents were mixed equally, a 20% reduction in rate occurred compared to the rate with the more dissolution-enhancing isolate alone. Rates in the presence of the more dissolution-enhancing isolate were reduced by up to 60% when cinnabar was pre-reacted with the isolate that enhanced dissolution to a lesser extent. All the data together imply that the property of DOM that enhances cinnabar dissolution is distinct from the property that causes it to sorb irreversibly to the cinnabar surface and lower the dissolution rate.