Natural Organic Matter on Redox Transformation and Complexation of Mercury under Dark, Anoxic Environments

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Naturally dissolved organic matter (DOM) is ubiquitous in water and sediment, affecting the redox transformation and speciation of metal contaminants such as mercury (Hg) in the environments. Depending on the redox state of DOM and the environmental condition, DOM can act either as an electron acceptor or an electron donor. Reduced DOM can transfer electrons to oxidized Hg(II) species to form elemental Hg(0), whereas oxidized DOM or DOM subunits may lead to the oxidation of Hg(0) and subsequently complex and stabilize Hg in the environment. In this study we investigate the role of DOM on the redox transformation and complexation of Hg under dark, anoxic conditions. We prepared reduced DOM isolates (both aquatic and terrestrial origins) by abiotic reduction using Pd-coated alumina as a catalyst and H_2 as an electron donor. We show that all DOM isolates were capable of rapidly reducing Hg(II) to elemental Hg(0) at relatively low DOM/Hg(II) ratios. However as DOM/Hg(II) ratios was increased, reduction of Hg(II) appeared to be inhibited as demonstrated by decreased production of purgeable Hg(0). This observation is consistent with the self competition of reduction and complexation of Hg by reactive functional groups in DOM (containing both reducing and complexing moieties). The reducing capacity varied among DOM isolates and depended on the Hg(II)/DOM ratio, with the highest value of about 8 μmol Hg/g C. The reduction of Hg(II) is also characterized by an initial rapid decrease in Hg(II) concentrations within the first 15 minutes followed by a slow rise of Hg(II) in 24 to 48 hours, suggesting that reduction is faster than the complexation. Our results indicate that DOM plays a dual functional role in the reduction and complexation of Hg, and the relevant reaction rates are likely control the redox cycle of Hg and its speciation in the anoxic environments.