Dissolved Organic Matter-Metal Interactions – Lessons Learned from the Study of Mercury

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Biogeochemical processes that influence the fate, bioavailability and transport of metals in aquatic systems are often mediated by interactions with dissolved organic matter (DOM). Beyond a general recognition of the importance of DOM in the environmental fates of metals, defining the roles played by DOM has been slow in coming due to the chemical complexity of DOM, the low concentrations of metals of interest, and the inherent complexity of natural systems. Recent advances in experimental design and analytical capabilities, however, are leading to greater process level understanding of these interactions, especially with regard to the biogeochemistry of mercury. DOM exerts controls on mercury biogeochemistry in two important ways. First, it acts as a strong ligand that, in the absence of sulfide, controls the mercury speciation in aquatic systems. The strength of DOM-mercury binding interactions is dependent on low-abundance reduced S groups (i.e., thiols, organic sulfides). Second, in the presence of sulphide, DOM interacts strongly with nanocolloidal HgS to stabilize HgS clusters and slow particle growth kinetics. Results from our studies using organic matter isolates suggest that nanocolloidal metacinnabar-like species become smaller and less ordered with decreasing Hg:DOM ratio, decreasing sulfide concentrations, and increasing DOM aromaticity. Subsequent studies have demonstrated the role of nanocolloidal phases of HgS in the methylation of Hg by sulfate-reducing bacteria, a previously unrecognized source of bioavailable Hg. In these studies, nanocolloidal HgS, the form of Hg anticipated to be found in the pore waters of sediments containing sulfide resulting from microbial sulfate reduction, was found to enhance Hg methylation, whereas larger HgS particles did not. Generally, methylation was greater in the presence of DOM with greater aromaticity. The results suggest that small, disordered HgS nanocolloids, stabilized against further aggregation by DOM, are bioavailable to Hg-methylating bacteria. The implications of these results for other metals (e.g. Cu, Zn) and inorganic nanomaterials will be addressed.