Mercury interactions with thiol ligands: implications for mercury methylation

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Methylmercury (MeHg) is a potent neurotoxin which bioaccumulates in aquatic food webs and in plants and causes adverse effects to human health and ecosystem sustainability. The formation of MeHg is predominantly a biotic process mediated by anaerobe bacteria where inorganic divalent Hg (HgII) is methylated intracellular. The formation of MeHg is thus largely controlled by factors influencing the availability of HgII to methylating bacteria. Recent studies have shown that HgII complexes with specific low molecular mass (LMM) thiols and with sulfide are available for bacterial uptake. Despite these scientific advances our understanding of the mechanisms controlling bioavailability and cellular uptake of HgII at the molecular level however remains limited.

We investigate how the stability constant of HgII complexes with LMM thiols depend on chemical structure of the thiol ligand. Experimental and modeling results coherently show that the presence of a primary amine group in the vicinity of the thiol group destabilizes the HgII-thiol complex. Based on these results we reevaluate the competition between HgII complexes with different thiol ligands (relevant for MeHg formation) and with inorganic sulfide.

We further explore how this competition control HgII availability for methylation, both in bacteria culture experiments and in boreal wetland soils. Our results show that the presence of LMM thiols exerts a complex control of HgII methylation in bacteria cultures by not only affecting the chemical speciation (and thus bioavailability) of HgII but also by other, yet unknown, mechanisms. Our results further suggest that in boreal wetlands predominantly HgII-LMM thiol complexes are methylated at concentrations of dissolved sulfide < 0.1 μM, whereas HgII-sulfide complexes (i.e. Hg(SH)2) are most important for HgII methylation at sulfide concentrations > 5 μM. In the intermediate sulfide concentration range both types of HgII species contribute to MeHg formation.