



Abiotic Production of Dimethylmercury in Aquatic Systems

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The biogeochemistry of Hg in the oceans and the bioaccumulation of MMeHg in its food webs are of particular interest given that marine fish are the major source of exposure of people to MMeHg. A distinct characteristic of the Hg biogeochemical cycle in the ocean is the occurrence of dimethylmercury (DMeHg), a highly toxic and volatile form of Hg. Reported concentrations of DMeHg in marine waters range from 0.01-0.4 pM and DMeHg has been found to constitute up to 80% of the methylated Hg pool (MMeHg + DMeHg). The underlying formation pathways of DMeHg in the ocean however remains unknown. For the Arctic system, where a significant fraction of the methylated pool is present as DMeHg, incubation experiments have shown the methylation rate for conversion of MMeHg to DMeHg to be one to two orders of magnitude higher than the methylation rate for inorganic Hg to DMeHg. Modelling work by Soerensen et al. further suggest in situ formation of DMeHg in sea water from MMeHg, rather than from inorganic Hg. Suggested pathways of DMeHg formation from MMeHg under environmentally-relevant conditions include reaction of MMeHg with hydrogen sulfide, selenoaminoacids and methylcobalamin. Formation of DMeHg from MMeHg reacted with L-cysteine has also been suggested, however supporting experimental data is lacking. Up to 90% of the CH₃Hg in marine waters, and over 99% of the CH₃Hg in sediments and inside cells, is adsorbed to reduced sulfur groups on mineral surfaces or bound to thiol groups within organic matter. Thus, surface mediated processes leading to DMeHg production could be of great significance. Here, we experimentally show that the methylation of MMeHg to DMeHg can be mediated by different sulfide minerals, of different thermodynamic stability, as well as by organic dithiol compounds. We also show that the reaction can take place on mineral surfaces in either artificial sea water and/or when algal cell components are present, suggesting that MMeHg could be methylated intracellularly by iron-sulfur clusters on protein surfaces.