

Degradation Pathways of Dimethylmercury in Natural Waters

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Abstract

Mercury (Hg) is a naturally occurring toxic trace metal whose release into the environment has been (and still is) exacerbated by human activities. The bioavailability of Hg is tied to its chemical speciation, with monomethylmercury (MMHg) being the primary form of Hg that bioaccumulates and biomagnifies. At the top of some food webs, MMHg can reach harmful levels. In addition to MMHg, a second methylated Hg species, dimethylmercury (DMHg), is found in aquatic environments. Dimethylmercury is especially abundant in the oceans, where it could potentially act as an important source of MMHg. The stability of DMHg in natural waters and which biogeochemical processes may be important for its degradation are poorly constrained. This knowledge gap could partially be related to the extreme toxicity and the volatility of DMHg, making it challenging to handle in the laboratory.

Through experimental studies, this thesis work has aimed to increase the understanding of DMHg cycling in the aquatic environment. Focusing on the stability and degradation of DMHg, abiotic pathways of DMHg degradation were explored. In **Paper I**, DMHg degradation via a novel sulfide-mediated pathway was demonstrated for both particulate and dissolved sulfide phases. Key aspects of the process were investigated through the manipulation of pH and DMHg:S ratios. In **Paper II**, the previously disputed process of aqueous photochemical decomposition of DMHg was confirmed for various natural and artificial water types. This process was studied further in **Paper III** by investigating the impact of dissolved organic matter and chloride on DMHg photodecomposition rates and the involvement of photochemically produced reactive intermediates. Monomethylmercury was the primary product of both sulfide-mediated decomposition and photodecomposition of DMHg. Rate calculations (**Paper I** and **II**) and comparison with MMHg photodecomposition (**Paper II** and **III**) confirm that both sulfide-mediated decomposition and aqueous photodecomposition of DMHg could be environmentally significant. **Paper IV** presents methods and considerations for laboratory work with DMHg, providing insights into both experimental and analytical aspects. This work demonstrates that DMHg can be analyzed together with MMHg and that significant safety risks of working with DMHg can be largely avoided. These insights are important as future work on DMHg is necessary to elucidate its role in aqueous Hg cycling in general and for MMHg cycling in particular.

Keywords: *Mercury, Marine, Degradation, Methylmercury, Aquatic.*

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