BIOTIC MERCURY METHYLATION IN SETTLING PARTICLES FROM THE WATER COLUMN OF AN OXIC FRESHWATER SYSTEM

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Introduction

Mercury (Hg) is a ubiquitous and hazardous trace metal. In particular, methylmercury (MeHg) is a neurotoxin that bioaccumulates in organisms and biomagnifies along the food web causing severe diseases in wildlife and human health (Mason et al., 2012). Aquatic environments are at the base of the MeHg transfer chain since this compound is synthesized in sub-oxic sediments by anaerobic microorganisms, such as sulfate-reducing bacteria (SRB) (Shao et al., 2012) and iron-reducing bacteria (IRB) (Fleming et al., 2006) and can be released to the water column through biogeochemical processes occurring in both sediment and water, and physical or biological transport mechanisms. Hg-methylation has been recently observed to occur in the oxic layer of the marine water column (Sunderland et al., 2009) which could represent a significant source of Hg to the food chain (Eckley & Hintelmann, 2006). However, no study showed that MeHg can be formed in settling particles of oxic lake waters. In this work we present results on Total-Hg (THg) and MeHg concentrations, and Hg methylation rates in settling particles and sediments of the largest oxic fresh-water lake in Western Europe (Lake Geneva), and we show that sulfate-reduction was linked to Hg methylation processes.

Methods

Settling particles were collected using a sediment trap system (Bloesch, 1996) placed 5 m above the sediment (actual sampling depth: 132 m). Surface sediments underneath the traps were recovered using two Mortimer gravity corers attached together from which the first centimeter was subsampled. Settling particles and sediments were spiked with $^{199}HgCl_2$ and $^{201}MeHgCl$ at concentrations similar to environmental levels. To better understand the role of anaerobic sulfate-reduction on the Hg-methylation, samples were also amended with MoO_4^{2-}, a specific inhibitor of the sulfate reducing metabolism (Fleming et al., 2006). Three control-replicate (no MoO_4^{2-} addition) and three molybdate-replicate (with MoO_4^{2-}) were incubated close to lake temperature (4°C) in the dark for 48h. The remaining sediment was used for further determination of potential Hg-methylation. Organic matter content was obtained by Rock-Eval 6 following the method described by Espitalie et al., 1985.

Results

Incubation results showed Hg methylation rate constants (k_m) were about 10-fold higher in settling particles than in sediments, and they were also observed to increase during the summer period. In addition, the percentage of ^{199}IHg methylated into $^{199}MeHg$ showed values that ranged between 3.0 and 12.7 %, which were similar to the ambient %MeHg/THg ratio found in the traps collected during a period of two years without incubation (0.4 – 9.6%), supporting that incubation experiments were comparable to in situ conditions. Molybdate amendments reduced by 80% the Hg-methylation rates in sediments and between 60% and 90% (k_m ~1.2 x 10^{-2} day^{-1}) in settling particles, and a positive correlation between Hg methylation rates and sulfate consumption was observed. Furthermore, C/N ratio, Hydrogen and Oxygen Indexes (HI and OI) were used as proxies of OM sources and biological and diagenetic alteration to better understand the differences between k_m and %MeHg/THg in sediments and settling particles. C/N results showed that OM in surface sediments was fresher in settling particles than in surface sediments, and HI and OI data supported that OM in settling particles were less degraded and more algal-type than in sediments.

Conclusion

Results suggest that methylation of Hg occurred in settling particles of Lake Geneva oxic water column. Indeed, higher Hg methylation rate constants compared to sediments were observed, likely due to the differences on the degradation state of the OM and anoxic microenvironments naturally created inside the settling aggregates. Thus, settling particles are a potentially important compartment for MeHg production in freshwater systems.

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