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Mercury methylation and demethylation in Hg-contaminated lagoon sediments (Marano & Grado Lagoons, Italy)

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ABSTRACT

Mercury (Hg) transformation activities and sulfate (SO_4^{2-}) reduction were studied in sediments of the Marano and Grado Lagoons in the Northern Adriatic Sea region as part of the "MIRACLE" project. The lagoons, which are sites of clam (*Tapes philippinarum*) farming, have been receiving excess Hg from the Isonzo River for centuries. Marano Lagoon is also contaminated from a chlor-alkali plant. Radiotracer methods were used to measure mercury methylation (^{230}Hg , ^{197}Hg), methylmercury (MeHg) demethylation (^{14}C -MeHg) and SO_4^{2-} reduction (^{35}S) in sediment cores collected in autumn, winter and summer. Mercury methylation rate constants ranged from near zero to 0.054 day^{-1} , generally decreased with depth, and were highest in summer. Demethylation rate constants were much higher than methylation reaching values of $\sim 0.6 \text{ day}^{-1}$ in summer. Demethylation occurred via the oxidative pathway, except in winter when the reductive pathway increased in importance in surficial sediments. Sulfate reduction was also most active in summer (up to $1600 \text{ nmol mL}^{-1} \text{ day}^{-1}$) and depth profiles reflected seasonally changing redox conditions near the surface. Methylation and demethylation rate constants correlated positively with SO_4^{2-} reduction and pore-water Hg concentrations, and inversely with Hg sediment–water partition coefficients indicating the importance of SO_4^{2-} reduction and Hg dissolution on Hg cycling. Hg transformation rates were calculated using rate constants and concentrations of Hg species. In laboratory experiments, methylation was inhibited by amendments of the SO_4^{2-} -reduction inhibitor molybdate and by nitrate. Lagoon sediments displayed a dynamic seasonal cycle in which Hg dissolution in spring/summer stimulated Hg methylation, which was followed by a net loss of MeHg in autumn from demethylation. Sulfate-reducing bacteria (SRB) tended to be responsible for methylation of Hg and the oxidative demethylation of MeHg. However, during winter in surficial sediments, iron-reducing bacteria seemed to contribute to methylation and Hg-resistant bacteria increased in importance in the reductive demethylation of MeHg. The high rates of MeHg demethylation in lagoon sediments may diminish the accumulation of MeHg.

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1. Introduction

Methylmercury (MeHg) is a potent neurotoxin that adversely affects brain development, especially in fetuses and young children (Clarkson, 2002). Much of the consumption of MeHg by humans is via fish, which bioaccumulate MeHg from the food web (Fitzgerald and Clarkson, 1991; Bloom, 1992). The global use of mercury (Hg) has decreased drastically in the past several years, but it remains

a threat due to releases from energy generation, incineration, and mobilization from mining activities (Fitzgerald, 1993). Mercury can also be transported hundreds of km from point sources, such as Hg mines, and this Hg can become bioavailable and methylated to MeHg, thus posing a threat to wildlife and humans (Hines et al., 2000).

Shallow coastal lagoons are ideal sites for the rapid methylation of Hg to MeHg, and its bioaccumulation in animal species consumed by humans. Lagoons are usually highly productive due to nutrient inputs from rivers and streams, they accumulate labile organic matter in sediments that fuels microbial processes responsible for Hg methylation, and they are often sinks for coastal

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