Methylation and Demethylation of Mercury Throughout the Idrija River System

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Abstract: The Idrija Mercury Mine was active for 500 years and Hg has been distributed throughout the system all the way to the northern Adriatic Sea over 100 km away. Total Hg and methylmercury (MeHg) vary greatly throughout the system, and sharp increases in both occur several tens of km for the mine, especially around impoundments and estuarine regions. Radiotracer methods were used to investigate Hg transformations throughout the system and almost every habitat studied actively transformed Hg. Reductive demethylation dominated in riverbanks, but methylation was noted as well. Sediments behind impoundments exhibited rapid methylation near the surface with reductive demethylation gradually replaced by the oxidative path with depth. Methylation was more active in estuarine sediments and demethylation was primarily via the oxidative pathway. MeHg concentrations were also much higher in estuarine sediments than in the upstream impoundment deposits. Mercury levels decreased offshore in the Gulf of Trieste, but dissolved species did not. Seasonal changes in redox and bioturbation in the Gulf affected Hg transformation rates and the relative importance of oxidative vs. reductive demethylation. The Idrija system is widespread and dynamic encompassing the gamut of Hg biogeochemistry.

Key words: idrija mine, methylation, demethylation, impoundments, marine sediments

INTRODUCTION

Five Hundred years of activity at the Idrija Mercury Mine has left a legacy of contamination along the 100 km route from the mine to the northern Adriatic Sea. Mercury concentrations are elevated in air, waters, sediments, and riverbanks, and mercury (Hg) is transformed in several different types of habitats throughout the system (HORVAT *ET AL.* 2002). However, mercury concentrations and speciation vary greatly along the path to the sea, and in some cases, both total Hg and methylmercury (MeHg) levels increase greatly several km from the mining region (HINES *ET AL*. 2000). This is especially noticeable in the middle and lower sections of the Soca/Isonzo River, and in the Isonzo estuary. In addition, the MeHg to total Hg ratio increases toward the sea, suggesting that MeHg formation is very active along the entire path, especially near impoundments and estuarine areas. To investigate the accumulation of MeHg in the Idrija system, Hg transformations were determined in different seasons in riverbank soils, in sediments in the Idrijca and Soča Rivers, and in sediments within the Isonzo estuary and several km into the Gulf of Trieste.

MATERIALS AND METHODS

Mercury methylation potentials were determined using ^{203}Hg and a toluene extraction procedure. MeHg demethylation potentials were determined using ^{14}C-MeHg and monitoring the production of $^{14}CH_4$ and $^{14}CO_2$ (HINES *ET AL.* 2000). Pore water (Hg, MeHg, nutrients, Fe, SO_4^{2-}, ΣH_2S) and solid phase (Hg, MeHg, organic C, N, S, reduced S) chemistry were also determined in many instances (HINES *ET AL*. 1997).

RESULTS AND DISCUSSION

Virtually every habitat studied had the potential to transform Hg to some degree. Sediments were primarily cobble in the 40 km stretch of the Idrija River prior to its confluence with the Soca River, and these deposits yielded little activity. However, riverbank soils in this reach actively transformed Hg with a dominance of demethylation (k_{deg} 0.9-5.5 % day^{-1}). Significant methylation was also noted (k_{meth} 0-0.6 % day^{-1}). The methyl group of MeHg was converted almost exclusively to CH_4 in these soils indicating that demethylation was catalyzed by an organomercurial lyase enzyme of the bacterial Hg detoxification system (*mer*) (BARKAY *ET AL.* 2003; MARVIN-DIPASQUALE *ET AL*. 2000).

Sediments behind a hydropower dam impoundment in the Soca River exhibited active methylation and demethylation of Hg, but methylation was restricted primarily to the upper few cm, which also displayed the highest concentrations of dissolved Hg (48 ng/L) and MeHg (6.7 ng/L) (Fig. 1). Demethylation was quite active with CH_4 accounting for >60 % of the C released at the surface and decreasing to ~10 % at 10 cm, suggesting that any contribution of

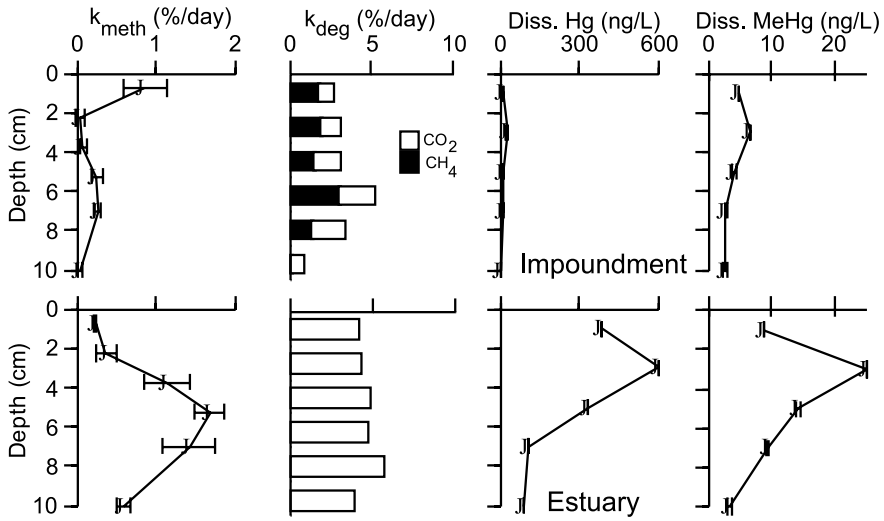

Figure 1. Depth profiles of methylation (k_{meth}) and demethylation (k_{deg}) rate constants, and dissolved total Hg and MeHg in freshwater sediments behind an impoundment and in estuarine sediments.

the reductive path to demethylation was decreasing with depth. The persistence of CH_4 release was probably also due to the dominance of methanogenesis, which produces some CH_4 during oxidative demethylation (MARVIN-DIPASQUALE *ET AL*. 2000).

Methylation activity in sediments collected in the estuarine region was more rapid than in the impoundment sediments with a subsurface maximum, and the ratio of methylation to demethylation (rate constants) was twice that noted in the freshwater impoundment muds (Fig. 1). All C released from MeHg during its degradation was recovered as CO_2 indicating that demethylation occurred entirely by the oxidative pathway. Dissolved total Hg was 10-20 fold higher in the estuarine pore waters (up to 600 ng/L) than in the freshwater sediments, and MeHg in estuarine pore waters was ~5-fold higher. The estuarine sediments contained a little more than 1.0 mM SO_4^{2-}, which decreased with depth, indicating that SO_4^{2-}-reducing bacteria were probably responsible the oxidative demethylation of MeHg as well as its formation. It has been shown that significant, but low concentrations of SO_4^{2-} enhance the formation of MeHg (GILMOUR *ET AL*. 1992).

Hg and MeHg levels in marine sediments decreased from the mouth of the Isonzo River into the central Gulf of Trieste (Hg_{tot} 45 to 1.0. µg/g; MeHg 4.0 to 0.2 ng/g), whereas dissolved Hg and MeHg did not vary significantly. Methylation and demethylation activity in marine sediments decreased with depth (Fig. 2), except in summer when a subsurface maximum was noted at the maximum depth of bioturbation (data not shown). The methyl group of MeHg was converted primarily to CO_2 in marine sediments, except for a slight production of CH_4 in surficial sediments in winter; a phenomenon that increased offshore inversely to rates of bacterial sulfate reduction (data not shown).

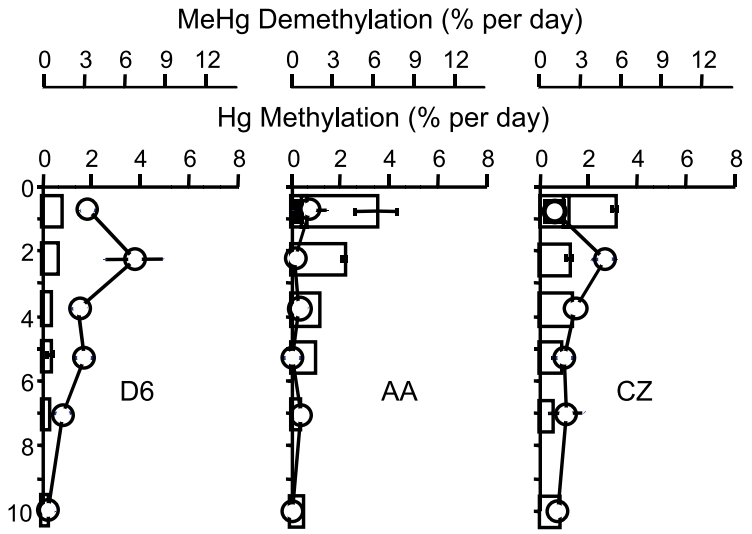

Figure 2. Depth profiles of mercury transformation rate constants at three sites in the Gulf of Trieste in March. Site D6 is closest to shore and the river mouth, CZ is most offshore. Black columns represent CH_4 and white CO_2 production during demethylation of MeHg