

Relationship between mercury species and solid sulfides in aquatic sediments

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Abstract: Distributions of total and methylmercury in sediment and porewater, as well as speciation of reduced sulfur species were investigated in different kinds of aquatic sediments (freshwater, estuarine and marine), characterized with a large range of mercury contamination level. Total mercury was found to be better correlated with CRS (chrome reducible sulfur), than with AVS (acid volatile sulfides). Methylmercury, both in sediments and porewater, was related to AVS and AVS/CRS ratio, as maximums of these species were obtained at the same sediment depths in the investigated sediment cores. Relationships obtained between mercury species (total and methylmercury) and reduced sulfur species in investigated sediments suggest that mercury in sediment is related to solid sulfides in several ways. Concentration of mercury species in the solid phase can be regulated by adsorption onto inorganic and organic reduced sulfurs in sediments. It is also possible that redox conditions and sulfur concentration/speciation where AVS are stabilized favor methylation over demethylation process, resulting in maxima of these species at the same sediment depths.

Key words: mercury, methylmercury, sediment, solid sulfides

INTRODUCTION

Distribution of mercury species in aquatic sediments should be related with solid reduced sulfur species (AVS – acid volatile sulfides and CRS – chrome reducible sulfur) due to, first, a high affinity of solid sulfides for mercury (GAGNON ET AL., 1997; MORSE AND LUTHER, 1999), and second, due to a common organism (sulfate reducing bac-

teria – SRB) responsible for production of sulfides and methylmercury (ULLRICH ET AL., 2001) in aquatic sediments. However, literature data demonstrating interaction of total mercury (HgT) and methyl mercury (MeHg) with solid sulfides in sediments are scarce and inconsistent. Some authors propose AVS as a sink for HgT in sediments (GAGNON ET AL., 1997) and others claim that HgT is preferably associated with CRS (HUERTA-DIAZ

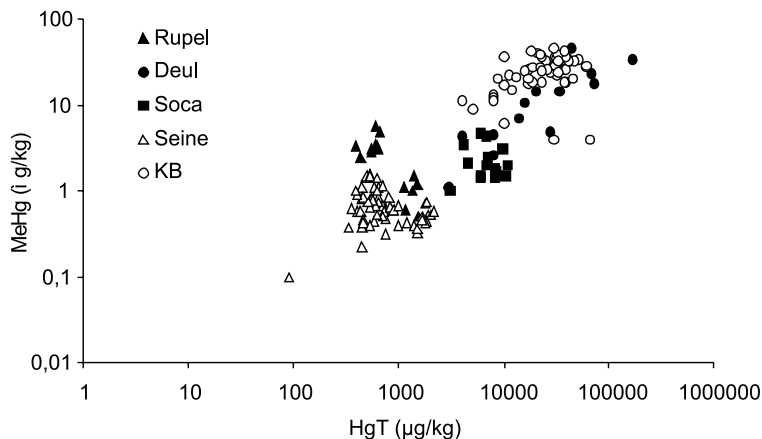


Figure 1. Total and methylmercury concentrations in sediments of the investigated areas.

AND MORSE, 1992) due to coprecipitation of Hg with pyrite. Data on the relation of MeHg and solid sulfides in sediments are practically absent from the literature.

In this work the relation between HgT and MeHg with AVS and CRS was studied in different types of aquatic sediments, characterized with a large range of mercury contamination level (Figure 1). They include marine sediment contaminated with mercury by chlor-alkali plant (Kastela bay, Croatia), estuarine sediment moderately polluted with mercury (Seine estuary, France), estuarine sediment highly polluted with mercury by mercury mine (Soca river, Slovenia), riverine sediment moderately polluted by mercury, but characterized with very high organic matter content (Rupel river, Belgium) and riverine sediment highly polluted with mercury by metallurgic industry (canal Deul, France). Sediment cores were sampled manually, sliced under inert atmosphere, porewater was isolated by centrifugation and both, solid and liquid phase analyzed for mercury and sulfur species. Mercury was analyzed by CVAFS method, methylmercury

by extraction, ethylation and GC-CVAFS detection and solid sulfides by standard methods (extraction with cold HCl for AVS and hot HCl + Cr (II) for CRS).

RESULTS AND DISCUSSION

Relationship between HgT and AVS was generally not established in the investigated sediments, but in some of them positive correlation was found between HgT and CRS suggesting that Hg may be more readily incorporated into pyrite than adsorbed onto amorphous Fe-monosulfides. According to MORSE AND LUTHER (1999), it is not clear if Hg in this fraction is present as discrete HgS phases or coprecipitated with FeS₂. In some of investigated sediments, very good correlations were established between MeHg and AVS, indicating, or an efficient adsorption of MeHg onto iron monosulfides, or something common in the mechanisms of their formation in sediments. Examples of MeHg, AVS and AVS/CRS ratio depth profiles obtained in sediment cores taken in the Seine estuary and in the Kastela bay are given in Figure 2.

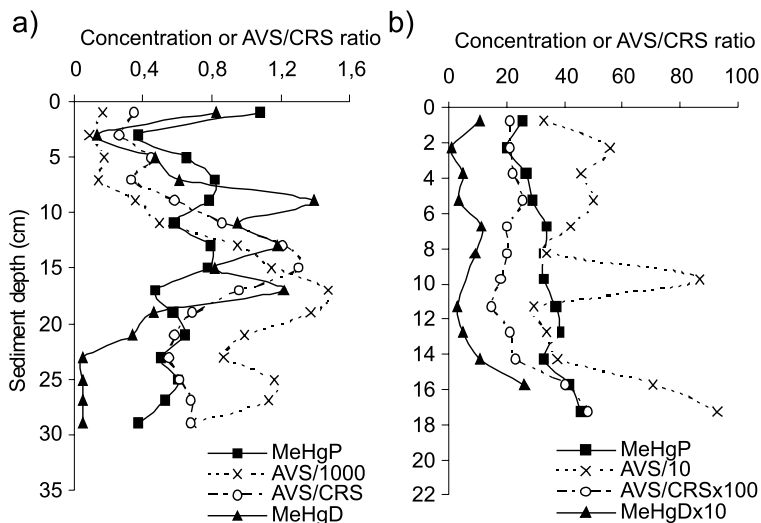


Figure 2. Distributions of particulate (MeHgP) and dissolved (MeHgD) methylmercury, AVS and AVS/CRS ratio in sediment cores taken in (a) Seine estuary in July 2001, and (b) Kastela bay in October 2001. (MeHgP in $\mu\text{g}/\text{kg}$; MeHgD in ng/l , AVS in mg/kg , AVS/CRS ratio calculated as $\text{AVS-Fe}/\text{CRS-Fe}$).

The AVS/CRS ratio indicates degree of conversion of AVS to CRS, where values higher than 1 (for AVS-Fe/CRS-Fe ratio) mean a low degree of conversion of AVS to CRS and stabilization of AVS. In aquatic sediments AVS/CRS ratio is generally low (<1) and depends on the concentration and form of sulfur and availability of reactive iron in sediment porewater (GAGNON ET AL., 1995). Both cores illustrate a good agreement between MeHg profiles in sediment and porewater with depth profiles of AVS and/or AVS/CRS ratio. In the Seine, sediment maximums of MeHgP and MeHgD correspond to maximum of AVS/CRS ratio and afterward MeHg levels decrease as concentration of AVS and AVS/CRS ratio decrease. In the Kastela Bay, sediment there is no pronounced MeHg maximum, but at greater depths both particulate and dissolved MeHg increase as AVS and AVS/CRS ratio increase. A relationship

found between dissolved MeHg and AVS/CRS ratio suggests that conditions in porewater, which are favorable for formation of AVS and their slow conversion to CRS (high AVS/CRS ratio), also offer favorable conditions for Hg methylation. Such conditions could be favorable for Hg methylation due to high activity of SRB (recognized by efficient formation of AVS), but also due to particular speciation of Hg in porewater at this depth and presence of Hg-sulfur species which are readily available for methylation. These conditions could correspond to the sulfide concentration and speciation where maximal concentration of neutral Hg-sulfur species (HgS^0), which are proposed as Hg form accumulated by SRB in sulfidic water (BENOIT ET AL., 1999), is presented.

In sediments of the Rupel and Soca rivers reduced organic sulfur species in the solid

phase were also measured and these preliminary results indicated that some fractions of organic sulfur (FAS – fulvic acid sulfur) could be also related to MeHg distribution in sediments.

CONCLUSIONS

Relationships obtained between mercury species (total and methylmercury) and reduced sulfur species in different kinds of aquatic sediment (freshwater, estuarine and marine) suggest that mercury in sediment is related to solid sulfides in several ways. Concentration of mercury species in the solid phase can be regulated by adsorption onto inorganic and

organic reduced sulfurs in sediments. It is also possible that redox conditions and sulfur concentration/speciation where AVS are stabilized favor methylation over demethylation process, resulting in maxima of these species at the same sediment depths. Better understanding of mechanism of these interactions would help us to explain better diagenesis of mercury in aquatic sediments.

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REFERENCES

- BENOIT, J. M., GILMOUR, C. C., MASON, R. P. HEYES, A. (1999): Sulfide controls on mercury speciation and bioavailability to methylating bacteria in sediment pore waters; *Environ. Sci. Technol.* 33, 951-957.
- GAGNON, C., MUCCI, A., PELLETIER, E. (1995): Anomalous accumulation of acid-volatile sulphides (AVS) in coastal marine sediment, Saguenay Fjord, Canada; *Geochim. Cosmochim. Acta* 59, 2663-2675.
- GAGNON, C., PELLETIER, E., MUCCI, A. (1997): Behaviour of anthropogenic mercury in coastal marine sediments; *Mar. Chem.* 59, 159-176.
- HUERTA-DIAZ, M. A. AND MORSE, J. W. (1992): The pyritization of trace metals in anoxic marine sediments; *Geochim. et Cosmochim. Acta* 56, 2681-2702.
- MORSE, J. W., LUTHER III, G. W. (1999): Chemical influences on trace metal-sulfide interactions in anoxic sediments; *Geochim. et Cosmochim. Acta* 63, 3373-3378.
- ULLRICH, S. M., TANTON, T. W., ABDRAHITOVA, S. A. (2001): Mercury in the aquatic environment: A review of factors affecting methylation; *Critical Rev. Environ. Sci. Technol.* 31, 241-293.