

Redox oscillation affecting mercury mobility from highly contaminated coastal sediments: a mesocosm incubation experiment

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Abstract. Mercury (Hg) mobility at the sediment-water interface was investigated during a laboratory incubation experiment on highly contaminated sediments (up to 23 $\mu\text{g g}^{-1}$) of the Gulf of Trieste. Undisturbed sediment was collected in front of the Isonzo River mouth, which inflows Hg-rich suspended material originating from the Idrija (NW Slovenia) mining district. Since hypoxic and anoxic conditions at the bottom are frequently observed, a redox oscillation was simulated in the laboratory at *in situ* temperature, using a dark flux chamber. Temporal variations of several parameters were monitored simultaneously: dissolved Hg and methylmercury (MeHg), O_2 , NH_4^+ , $\text{NO}_3^- + \text{NO}_2^-$, PO_4^{3-} , H_2S , dissolved Fe and Mn, dissolved inorganic and organic carbon (DIC and DOC). Benthic fluxes of Hg and MeHg were higher under anoxic conditions while re-oxygenation caused concentrations of MeHg and Hg to rapidly drop, probably due to re-adsorption onto Fe/Mn oxyhydroxides and enhanced demethylation. Hence, during anoxic events, sediments of the Gulf of Trieste may be considered as an important source of dissolved Hg species for the water column. However, re-oxygenation of the bottom compartment mitigates Hg and MeHg release from the sediment, thus acting as a natural "defence" from possible interaction between the metal and the aquatic organisms.

Key words: Mercury, sediments, benthic chamber, incubation

Introduction

The Gulf of Trieste (northern Adriatic Sea) has been affected by mercury (Hg) inputs from the Isonzo River, the largest contributor of this metal into the northern Adriatic Sea since the 16th century, due to its transport of cinnabar (HgS) rich tailings from the Idrija (Slovenia) mining district (Covelli et al., 2001). Mercury is still delivered to the nearby Gulf of Trieste (Horvat et al., 1999; Faganeli et al., 2003; Covelli et al., 2006, 2007), where bottom sediments show Hg concentrations ranging from 0.10 to 23.3 $\mu\text{g g}^{-1}$ against an estimated natural background of 0.13 $\mu\text{g g}^{-1}$. Hypoxic/anoxic conditions at the sediment - water interface (SWI) have been observed in the Gulf of Trieste, as a consequence of high loadings of nutrients and organic matter and strong late summer water stratification (Faganeli et al., 1991). Under such environmental conditions, sediments could act as a significant source of *in situ* Hg methylated species

(Fitzgerald et al., 2007; Merritt and Amirbahman, 2009). By means of an incubated benthic chamber it is possible to observe, under controlled laboratory conditions, the effects of O_2 depletion on the biogeochemical behavior of the benthic compartment (Ogrinc and Faganeli, 2006; Covelli et al., 2008; Emili et al., 2011).

The aim of this study was to evaluate Hg and MeHg cycling at the SWI in the Gulf of Trieste in case of anoxic events, simulating an oxic/anoxic transition in a dark incubated benthic chamber, at *in situ* temperature. To this purpose, a volume of undisturbed sediment was sampled from an experimental site located in front of the Isonzo River mouth (Fig. 1), where an elevated Hg content was expected, on the basis of previous investigations (Covelli et al., 2001). In addition to Hg species, water samples were also analyzed for H_2S , nutrients (N and P), Fe and Mn, dissolved inorganic and organic C (DIC and DOC), to better understand the redox processes occurring in the incubated system.



Fig. 1. Location of the sampling station (Gulf of Trieste, Northern Adriatic Sea, Italy).

Materials and Methods

Bottom sediment and the overlying water were collected by a SCUBA diver in June 2010, using a cylindrical Plexiglas chamber as a sampler ($h = 25$ cm, i.d. = 24 cm). The chamber was carefully transported to the laboratory where the overlying water was replaced by *in situ* collected bottom seawater. The chamber was sealed and placed in a dark room at *in situ* temperature (24°C) for incubation (Fig. 2).

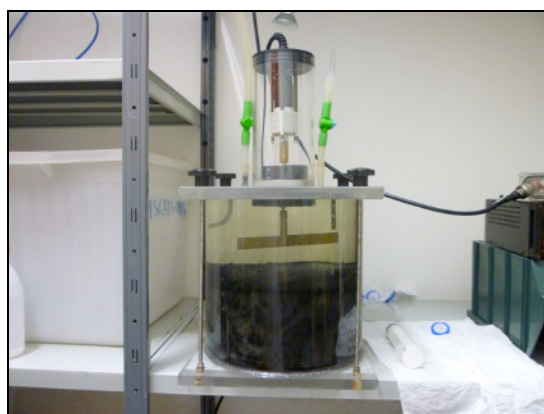


Fig. 2. The incubated benthic chamber with its stirring mechanism.

After 27 days, the system was re-oxygenated by opening the chamber and leaving the water surface in contact with the atmosphere for 7 days. Throughout the incubation experiment, water samples were periodically collected from the chamber using a plastic syringe and the withdrawn volume of water was compensated by *in situ* collected bottom seawater. Prior to each sampling, the system was homogenized for 15 min by means of a magnetic stirrer.

Dissolved O_2 was determined by the Winkler method (Grasshoff et al., 1983) using an automated titration system (Mettler Toledo DL 21). Determination

of H_2S was performed spectrophotometrically after trapping with Zn acetate (Grasshoff et al., 1983). Other parameters in the dissolved phase were determined on samples filtered through a Millipore Millex HA $0.45 \mu\text{m}$ filter. DIC and DOC determinations were performed using a Shimadzu TOC 5000A analyzer. Dissolved Fe and Mn were determined by GFAAS (Perkin Elmer 5100PC) using $\text{Mg}(\text{NO}_3)_2$ as a matrix modifier. Nutrients were determined according to Grasshoff et al. (1983) using a continuous flow segmented system (Bran-Luebbe AAQuattro).

Total Hg in the solid phase was determined by CVAAS (Perkin Elmer AAnalyst 100-FIAS) after a total decomposition of the sample with a mixture of HF + *aqua regia* in a closed microwave system (Milestone MLS 1200). Total dissolved Hg determination was performed according to Horvat et al. (1991): after exposure to UV light and oxidation with BrCl ($0.5 \text{ mL}/100 \text{ mL}$ sample), pre-reduction ($\text{NH}_2\text{OH}\cdot\text{HCl}$, 0.25 mL 30%) was followed by reduction with SnCl_2 and Au trapping. Analyses were performed by a Brooks Rand CVAFS. MeHg analyses were conducted according to Horvat et al. (1993a,b) and Liang et al. (1994a,b). After distillation, water samples were ethylated ($\text{pH } 4.6$, $100 \mu\text{L}$ of acetate buffer, $50 \mu\text{L}$ NaBeT_4 1%), recollected on Tenax traps at room temperature ($t = 15$ min, Hg-free N_2), and thermally desorbed ($T = 180^{\circ}\text{C}$). Separation of the ethylated species was performed on a GC column. Mercury species were converted to Hg^0 by pyrolysis at 600°C and measured by CVAFS. Recovery of MeHg was estimated in each batch of analyses by spiking the samples with a known amount of MeHg in aqueous solution prior to distillation and analysis.

Results and Discussion

The average total Hg content in the surficial sediment (0-3.5 cm) was about $12 \mu\text{g g}^{-1}$, compared to the $> 30 \mu\text{g g}^{-1}$ maximum concentration reported in Hines et al. (2006).

An O_2 concentration $< 32 \mu\text{mol L}^{-1}$ (1 mg L^{-1}) was considered the limit for the hypoxic/anoxic transition. After 7 days of incubation, O_2 in the benthic chamber was no more detectable (Fig. 3). Oxygen was resupplied to the system by opening the benthic chamber after 27 days of incubation. As a consequence, O_2 concentration quickly rose to $142 \mu\text{mol L}^{-1}$, reaching a maximum of $291 \mu\text{mol L}^{-1}$ which was similar to the concentration values observed at the beginning of the experiment. During the oxic/anoxic transition, early diagenetic processes of organic matter consumption caused the remineralization of nutrients and the release of Fe/Mn and Hg species from the sediment.

MeHg was almost undetectable (0.03 ng L^{-1}) at the beginning of the experiment, and it rose to a maximum of 39 ng L^{-1} during the early stages of anoxia (Fig. 3). After 20 days of incubation, still under anoxic conditions and before reoxygenation, MeHg decreased to about 22 ng L^{-1} . After reoxygenation, MeHg quickly disappeared from the water column, decreasing to 0.3 ng L^{-1} at the end of the experiment. H_2S paralleled MeHg behavior, rising from $0.36 \mu\text{mol L}^{-1}$ at $t=0$ to a maximum of $75 \mu\text{mol L}^{-1}$ after

20 days of incubation. After that, H₂S concentration decreased, reaching undetectable levels after the reoxygenation of the system. Manganese was released from the sediment already at the beginning of the experiment, when O₂ depletion was slowly ongoing. The quick drop in concentration following reoxygenation suggests that Mn oxides were formed, possibly removing from solution other solutes (like MeHg) by coprecipitation. The observed behavior of H₂S and MeHg suggests that Hg methylation by sulfate-reducing bacteria (Compeau and Bartha, 1985) was active in the incubated sediment and that the hypoxic/anoxic conditions induced in the system favored methylation processes, as long as

H₂S concentration in the water column was below 80 μmol L⁻¹. After the optimum in sulfate reduction and the corresponding methylation processes, the system buffered both H₂S and MeHg concentrations and the species were removed from solution, possibly by precipitation of insoluble sulfides (Benoit et al., 1999). The sudden disappearance of H₂S and MeHg from the water column following the system reoxygenation suggests that Hg methylation in the incubated sediment is strongly dependant on the redox conditions of the system. Oxygen depletion triggers Hg methylation and MeHg is removed from the water column when oxic conditions are restored.

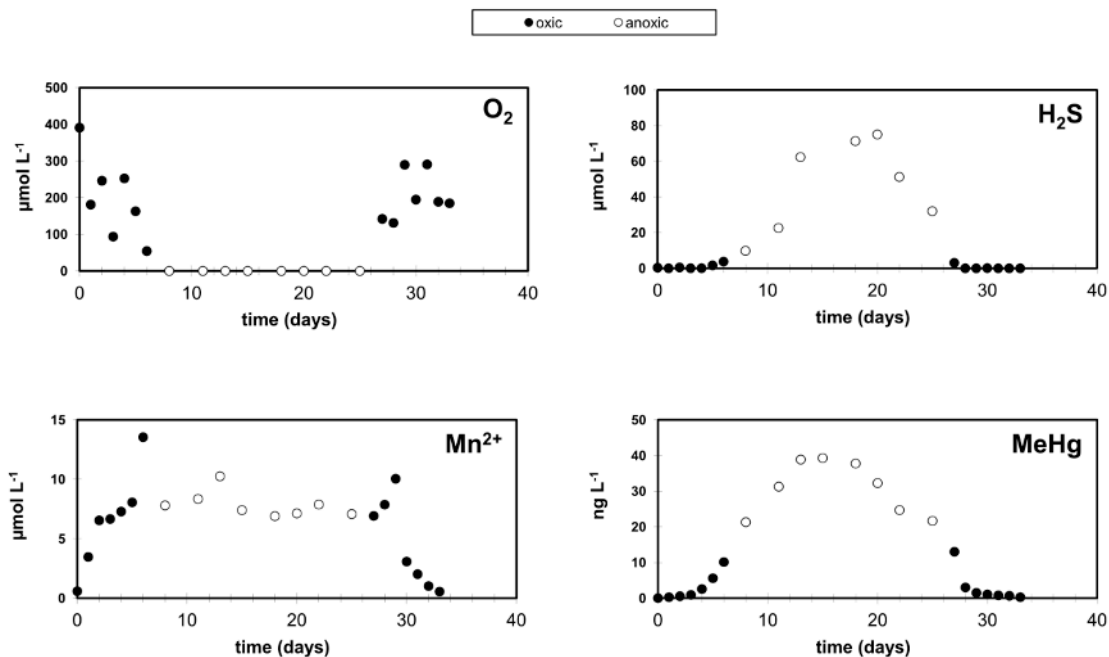


Fig. 3. Variation of solutes (O₂, H₂S, Mn²⁺, MeHg) concentration with incubation time. Black dots represent the oxic phase of the experiment, white dots represent the anoxic phase.

Conclusion

Hypoxic and anoxic conditions play a significant role in the remobilization of Hg from sediments at the Isonzo River mouth in the Gulf of Trieste. The increasing sulfide concentration in the benthic chamber is well correlated with the parallel increase in MeHg, in accordance with the hypothesis of Hg methylation being related to SO₄²⁻ reduction in anoxic sediments. The observed effects of sediment reoxygenation on the solutes concentrations suggest that reversion to oxic conditions removes Hg species from the water column, most probably through precipitation and coprecipitation with Fe and Mn oxyhydroxides. These findings are useful to understand Hg cycling at the SWI during hypoxic/anoxic events and the fate of Hg species following the restoration of the normal oxygenation conditions of the bottom waters.

Acknowledgements

The authors would like to thank Michele Giani and

Cinzia De Vittor of OGS-BIO Trieste for H₂S and DIC analyses. L.C. kindly acknowledges a predoctoral fellow-ship (programa I3P) from the Consejo Superior de Investigaciones Científicas (CSIC, Spain).

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