

BENTHIC FLUXES MEASUREMENT OF MERCURY AND METHYLMERCURY IN PIALASSA BAIONA (RAVENNA, ITALY)
FLUX BENTHIQUES DE MERCURE ET DE MÉTHYLMERCURE DANS LA RÉGION DE PIALASSA BAIONA (RAVENNE, ITALIE)

FLUSSI BENTICI DI MERCURIO E METILMERCURIO IN PIALASSA BAIONA (RAVENNA, ITALIA)

Stefano Covelli ^{(1)*}, **Andrea Emili** ⁽¹⁾, **Alessandro Acquavita** ^{(1) e (2)},
Enrico Dinelli ⁽³⁾, **Neža Koron** ⁽⁴⁾, **Jadran Faganeli** ⁽⁴⁾

⁽¹⁾ Department of Geosciences, University of Trieste, Italy

⁽²⁾ Environ. Prot. Agency of Friuli Venezia Giulia (ARPA FVG), Palmanova, Italy

⁽³⁾ Interdip. Center for Research on Environ. Sci. (CIRSA), University of Bologna, Italy

⁽⁴⁾ Marine Biological Station, National Institute of Biology, Piran, Slovenia

*Corresponding author: covelli@units.it

Abstract

Previous research on mercury (Hg) showed strong contamination of the Piallassa Baiona (P.B.) lagoon, near Ravenna. The lagoon received between 100 and 200 tons of Hg generated by an acetaldehyde factory in 1957-1977. In this study, the Hg cycling at the sediment-water interface in the P.B. lagoon was investigated by means of an *in situ* benthic chamber. The 8-h integrated flux of the methylated form was extremely low and estimated to be only 7% of the result obtained for a summer experiment performed in a similar Hg-contaminated environment (Grado lagoon). Conversely, the *in situ* flux of Hg accounted for a comparable amount to that observed in the Grado lagoon, although Hg contents in its sediments are almost 50% lower than in P.B. lagoon. Hg mobilization and sequestration in the system, limiting its bioavailability despite the high contents of metal buried in the bottom sediments, seem related to extremely anoxic conditions.

Keywords: *mercury; contamination; sediment; benthic fluxes; biogeochemical cycling*

Résumé

Des recherches précédentes sur le mercure (Hg) ont mis en évidence un taux de contamination élevé de la lagune de Piallassa Baiona (P.B.), près de Ravenne. Entre 1957 et 1977, la lagune a accumulé 100 à 200 tonnes de mercure issues d'une usine d'acétaldéhyde. Cette étude reconstitue la remobilisation du Hg à l'interface eau-sédiments à l'aide d'une chambre benthique *in situ*. Le flux quotidien (8 heures) de la forme méthylée obtenue est extrêmement bas, soit 7% de la valeur mesurée expérimentalement dans la lagune de Grado (Italie), aussi contaminée au Hg. Le flux total *in situ* de Hg est en revanche comparable, bien que son contenu dans les sédiments de Grado soit inférieur de pratiquement 50% à celui de P.B. Malgré des concentrations élevées en Hg, les conditions extrêmement anoxiques du

milieu semblent liées à la mobilisation et à la séquestration du Hg dans le système, ce qui en limite la biodisponibilité.

Mots-clés: *mercure; contamination; sédiment; flux benthiques; cycle biogéochimique*

Riassunto

Precedenti ricerche sul mercurio (Hg) hanno evidenziato un elevato stato di contaminazione della Pialassa Baiona (P.B.) presso Ravenna. La laguna è stata interessata da un apporto di Hg (100-200 tonn) prodotto da una fabbrica di acetaldeide nel periodo 1957-1977. In questo studio, è stata indagata la rimobilizzazione del Hg all'interfaccia acqua-sedimento per mezzo di una camera benthica *in situ*. Il flusso giornaliero (8 ore) per la forma metilata si è rivelato estremamente basso, pari al 7% di quanto osservato sperimentalmente in un ambiente simile contaminato da Hg, la laguna di Grado. Viceversa, il flusso di Hg totale è risultato comparabile a quanto osservato in laguna di Grado sebbene il contenuto di Hg nei sedimenti fosse inferiore di ca. 50% rispetto alla Pialassa. Mobilizzazione ed accumulo del Hg nel sistema, che limitano la biodisponibilità a dispetto delle elevate concentrazioni di Hg nei sedimenti, appaiono relazionati dalle condizioni anossiche del sedimento.

Parole chiave: *mercurio; contaminazione; sedimento; flussi benthici; ciclo biogeochimico*

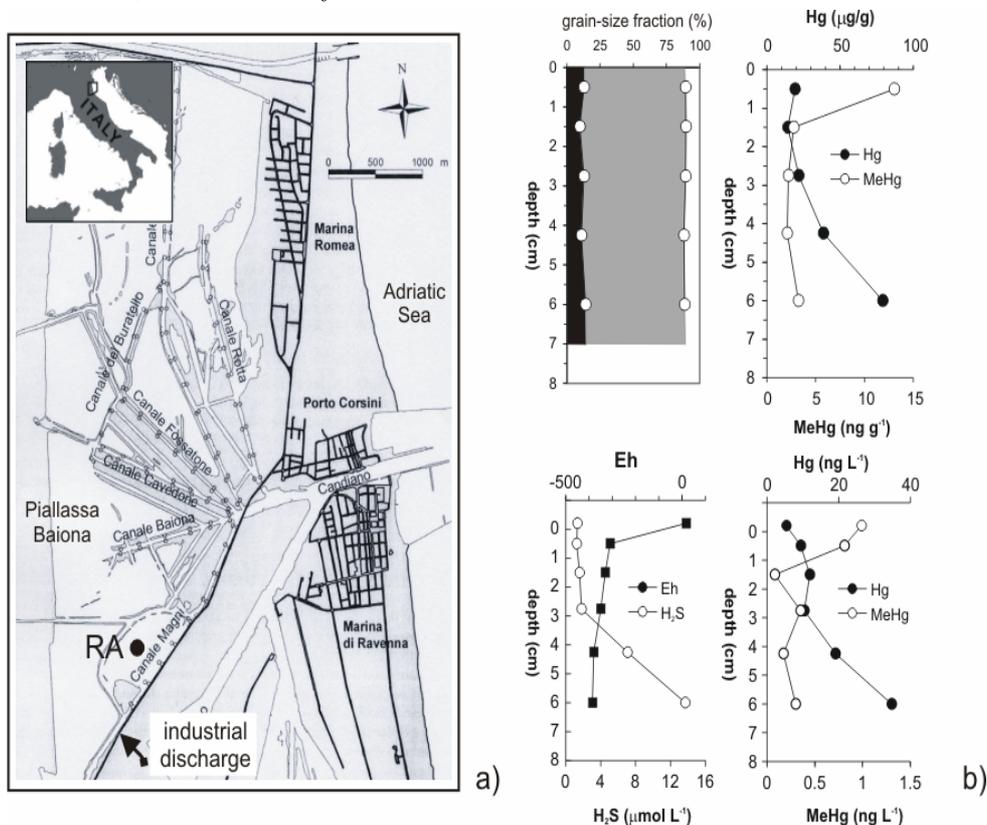
Introduction

The northern Adriatic coastal zone has been recognized as the most mercury (Hg) enriched environment within the whole Mediterranean basin (e.g. Covelli et al., 2001 and references herein). Bottom sediments represent an important “reservoir” and, potentially, a secondary source of Hg contamination, through sediment-water exchange followed by bioaccumulation in the food chain. Industrial activity has often been claimed as the main contributor to extremely high Hg concentrations in lagoon sediments, such as in the Venice lagoon (Bloom et al., 2004; Berto et al., 2006; Zonta et al., 2007) and in the Grado and Marano lagoons (Brambati, 2001; Piani et al., 2005). The small Ravenna lagoon (locally called Pialassa Baiona) received between 100 and 200 tons of Hg, discharged by a local acetaldehyde factory during the period 1958-1978. Almost 80% of the discharged Hg was accumulated in the sediments of the southern ponds (Miserocchi et al., 1993) where Hg bioaccumulation in Manila clams and transplanted mussels was also observed (Trombini et al., 2003; Cattani et al., 1999). This study aims to investigate Hg mobility at the sediment-water interface in the P.B. lagoon using *in situ* measurements of benthic fluxes. Results are compared with the Grado lagoon (Covelli et al., 2008), where Hg in the sediments is supposed to be mainly geogenic sulphide (cinnabar) transported by riverine suspended particles (Covelli et al., 2007).

Materials and methods

Field and laboratory operations. Sediment core sampling and benthic chamber experiments were performed in September 2009 at the Chiaro Magni pond (60 cm of depth, in Fig.1a). Sediment cores were collected by a diver, using a Plexiglas liner (16 cm i.d; 30 cm length). To preserve the original redox conditions the cores were extruded and sliced in a N₂-filled chamber, after supernatant water collection, and Eh was measured. Porewaters were extracted from the sediment by centrifugation at 3500 rpm for 40 min at in situ temperature, filtered on 0.45 µm pore size, collected in acid-pre-cleaned vials and finally frozen until analysis. Solid phase samples were freeze-dried, homogenized and sieved before analysis. The benthic chamber consists of a 50x50x30 cm plexiglas box, open at the bottom and equipped with a stirring mechanism. Water samples were collected from the chamber, at 2 hours time intervals (from t₀=0 to t_{final}=8h) and all samples were filtered except for dissolved oxygen (O₂). Salinity and temperature were measured in surface and bottom waters at every sampling, along with pH and Eh values inside the chamber.

Figure 1 – a) Location of the experimental site RA in the study area; b) vertical profiles of grain-size, Eh, total Hg and methylmercury in the solid phase and in the porewaters and dissolved H₂S contents in the first centimetres.



Analyses. Dissolved O₂, dissolved inorganic (DIC) and organic (DOC) carbon, and H₂S were determined according to Grasshoff et al. (1983). Total Hg (THg) in the dissolved phase was determined according to Horvat et al. (1991), while methylmercury (MeHg) in water and sediment samples followed Horvat et al. (1993a,b) and Liang et al. (1994a,b) using an LCD Milton Roy CVAFS. THg in the solid phase was determined by CVAAS on mineralized samples. Mineralization was performed in a closed microwave system (Milestone MLS-1200) using a mixture of 1.5 ml HF and 5ml *aqua regia*. Sediment grain-size was obtained by a laser granulometer (Malvern Mastersizer) while organic C (C_{org}) and total N (N_{tot}) content were determined by a Perkin Elmer 2400 CHN Elemental Analyzer after acidification of samples with 1 M HCl (Hedges and Stern, 1984). Trace and major elements compositions were obtained by X-Ray Fluorescence Spectrometry (XRF Philips PW 1480) on pressed powder pellets, following the matrix correction method of Leoni et al. (1986).

Results and discussion

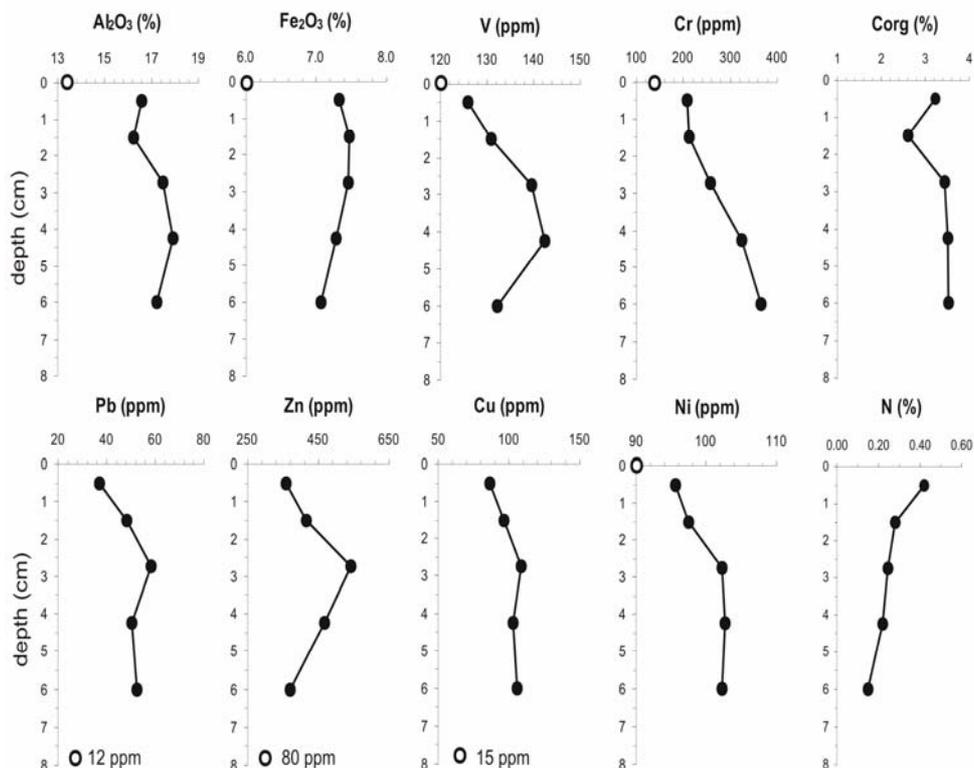
Solid phase and porewaters. Surface sediment at the RA experimental station (Fig. 1b) is rather uniform and it largely consists of fine particles (muds > 80%). The concentration of Hg in the solid phase increases significantly with depth, from 20 to 80 µg g⁻¹. There is no correlation with grain-size, as a consequence of the historical discharge of Hg which accumulated in sediments in a relatively short time interval, more than 40 years ago. Up to 1114 µg g⁻¹ of Hg were reported in subsurface sediments of the southern ponds (Miserocchi et al., 1993). Despite the elevated Hg content, MeHg accounts for a very small fraction (0.07-0.004%) of total Hg in the solid phase. As already reported in literature, there is no linear correlation between the two parameters, which means that MeHg production is not strictly dependent on total Hg content. Bottom sediments recorded the anthropogenic contribution of other heavy metals too (Fig. 2). V, Cr, Ni and, more significantly, Pb, Zn and Cu are higher than the average local background values (Amorosi et al., 2002; Curzi et al., 2006). However, in terms of bottom sediments contamination, a slight decrease is evident in the first centimetres, thus suggesting a recent recovering of the environment is taking place, which is not related to a change in grain-size.

The amount of C_{org} is rather constant in the sediments, whereas the observed decrease of N with depth could be due to a partial rimineralization of this component of the organic matter compared to C_{org}.

THg in porewaters (9.4-34.8 ng L⁻¹) increases downcore (Fig. 1a). Conversely, MeHg (0.17-0.81 ng L⁻¹) shows higher values in the 0-1 cm level, decreasing downcore. This trend would suggest that Hg methylation rather occurs at the sediment-water interface, and it is not affected by bioturbation. Sediments appeared to be extremely anoxic, except for a thin surficial oxidized layer. Eh varied from about 20 mV in the supernatant water to almost -400 mV downcore, which is consistent with sulphate-reduction conditions and the evidence of H₂S in porewaters at the deepest levels. High sulphide contents, due to active sulphate

reduction in the sediments, would probably limit Hg mobilization and methylation with the precipitation or adsorption of Hg on authigenic pyrite (Fabbri et al., 2001).

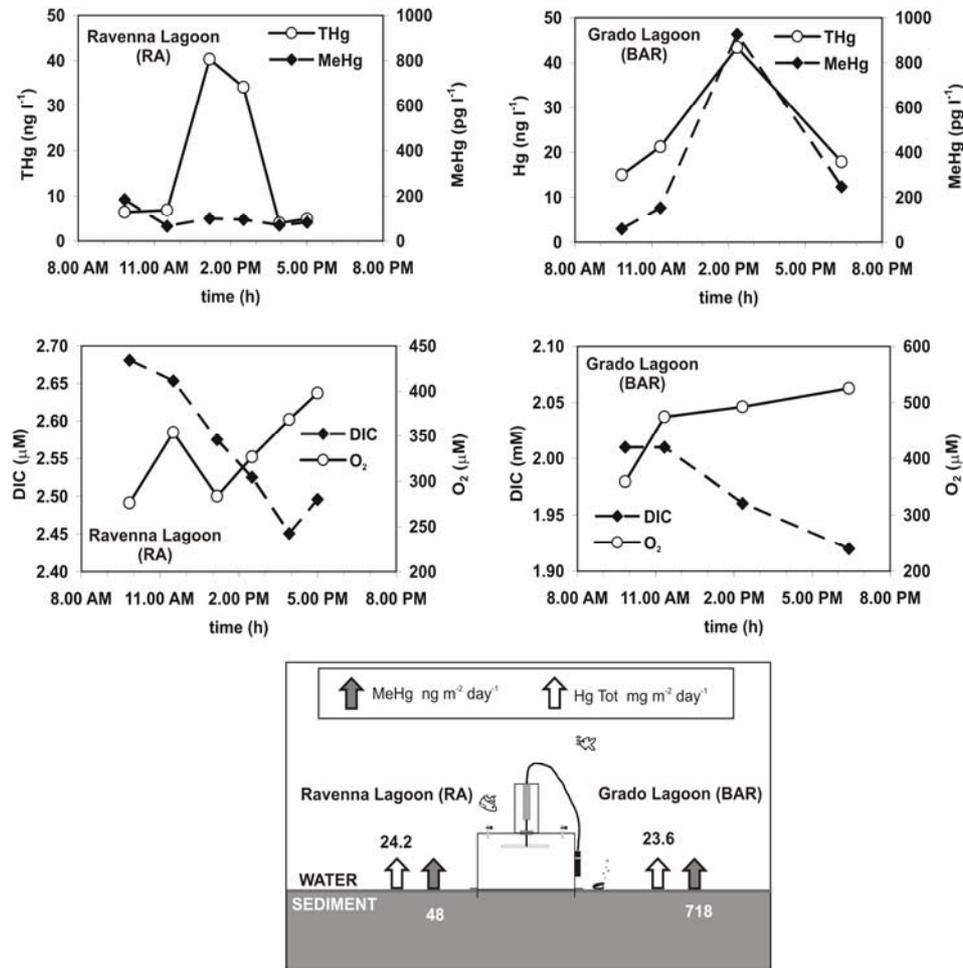
Figure 2 – Vertical profiles of some major and trace elements in core sediments of the RA experimental site. Open circles indicate local background values from the literature.



Benthic chamber experiment. Hg mobility at the sediment-water interface seems to be influenced by the photoperiod. Hg concentration shows a peak (40.4 ng L^{-1}) during the central hours of the day, while MeHg is rather constant (avg, 83 pg L^{-1}) with a slight increase corresponding to total Hg peaking. To better understand the biogeochemical benthic behaviour in RA, we compared our results with another lagoon environment, the Grado Lagoon (station BAR), where similar in situ investigations were conducted (Covelli et al., 2008). BAR showed a similar trend in oxygen and DIC compared to RA, with higher values for dissolved oxygen. Photosynthesis in BAR is more intense and the general redox conditions of the site appear to be more oxic. Although BAR sediments show lower Hg content ($10.7\text{-}13.7 \text{ } \mu\text{g g}^{-1}$), Hg concentrations in the water column (43.4 ng L^{-1}) are similar to RA, peaking in the central hours of the day. Conversely, MeHg in the benthic chamber is much higher in BAR (927 pg L^{-1}).

Diurnal fluxes of Hg and MeHg across the sediment-water interface were assessed by integrating the area under the curve defined by the variation of concentration with time.

Figure 3 – Concentration of some chemical parameters (THg, MeHg, DIC and O₂) versus time during the benthic chamber experiment in the Ravenna Lagoon (RA site) and in the Grado Lagoon (BAR site, Covelli et al., 2008); diurnal fluxes of THg and MeHg in the two lagoon environments are reported in the picture below.



Comparing RA and BAR fluxes it appears that Hg mobility is similar in the two sites ($\sim 24 \mu\text{g m}^{-2} \text{day}^{-1}$), despite a higher Hg content in the RA sediment; MeHg release is much higher in BAR ($718 \text{ ng m}^{-2} \text{day}^{-1}$, compared to $48 \text{ ng m}^{-2} \text{day}^{-1}$ in RA).

These results suggest that Hg methylation in RA is inhibited, probably due to strong anoxic conditions in the sediment and the formation of less bioavailable Hg species, such as sulphides, which limit Hg availability to methylating bacteria. Thus, sulphides in porewaters limit Hg availability and its release into the water column.

Conclusions

Although direct methylation/demethylation activity rates are lacking, strong anoxic conditions in the Ravenna Lagoon sediments seem to limit Hg availability and MeHg release if compared to a similar environment (Grado Lagoon), in spite of higher Hg contents. Thus, the potential risk associated with high Hg contamination of the Pialassa Baiona sediments seems to be partially mitigated, resulting in lower than expected Hg and MeHg fluxes.

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