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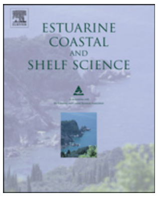

Benthic flux measurements of Hg species in a northern Adriatic lagoon environment (Marano and Grado Lagoon, Italy)

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ABSTRACT

As part of the "MIRACLE" project, the biogeochemical cycling of mercury (Hg) at the sediment–water interface was studied in the field in the Marano and Grado Lagoon (Northern Adriatic Sea). Seasonal investigations were conducted at selected experimental sites, where Manila Clams (*Tapes philippinarum*) were previously seeded. Measurements were performed seasonally during three campaigns, using two benthic chambers, one transparent and one dark, to evaluate the effect of light on Hg cycling. Total dissolved Hg (THg), methylmercury (MeHg), and dissolved gaseous Hg (DGM) species were considered. Diurnal benthic fluxes were found to significantly exceed the diffusive fluxes at all stations. The assessment of the annual recycling of Hg species from sediments to the water column showed that up to 99% of MeHg is recycled annually to the water column, while Hg recycling ranges from 30 to 60%. MeHg poses the higher risk for potential bioaccumulation in clams, but it is partially mitigated by Hg reduction, which seems to be an important process leading to evasion losses of Hg from these environments. Estimated benthic fluxes suggest that Hg recycling at the sediment–water interface is more active in the Grado sector. Hence, based on the estimated release of MeHg from sediments, it is suggested that the western sector seems to be more suitable for clam farming and the extension of rearing activities.

1. Introduction

Coastal areas throughout the world are increasingly exposed to a variety of organic and inorganic pollutants, due to the growing pressure of human activities. On the other hand, these environments are often protected by special laws and constitute important resources of great ecologic, recreational and economic value. In particular, fishing and rearing are widespread and commercially relevant activities for local inhabitants.

The edible species *Tapes philippinarum* (Manila Clam) was introduced (1983) to the Northern Adriatic lagoons as a commercially exploitable fishery resource. Nowadays, clam farming is widespread in the Venice Lagoon (Sfriso et al., 2008) and it is allowed in limited areas of the Marano and Grado Lagoon (Sladonja et al., 2011). Although the Marano and Grado Lagoon is included in the "Natura 2000" network because of the value of its habitats, a large area in the middle of the Lagoon (13,500 ha), roughly corresponding to the influence of the Aussa–Corno river system (Fig. 1), has been declared a "contaminated site of national interest" by the Italian authorities (Ramieri et al., 2011). This is mainly the consequence of mercury-contaminated sediments, originating from both mining and industrial sources (Covelli et al., 2009 and reference therein).

Mercury (Hg) is a highly toxic heavy metal, with a complex biogeochemical cycle that involves its transformation into the more toxic and potentially bio-accumulable organo-metallic form methylmercury (MeHg) (Fitzgerald et al., 2007; Merritt and Amirbahman, 2009). Because of this, the evaluation of Hg mobility is of great concern in the coastal marine environment (Rothenberg et al., 2008), together with the mechanisms involved in the production and/or release of MeHg from contaminated sediments into the water column (Han et al., 2007; Hines et al., 2012), especially where rearing activities are performed or planned (Bloom et al., 2004a).

Measurements of *in situ* benthic fluxes are commonly used to evaluate the release of mercurial species from contaminated sediments (Covelli et al., 1999, 2008, 2011; Gill et al., 1999; Choe et al.,

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Fig. 1. The Marano and Grado Lagoon (Northern Adriatic Sea): schematic representation of the study area. Red squares indicate the location of the sites chosen for the benthic chamber deployments: MB and MC (this study); ART (Artalina) and BAR (Barbana) (Covelli et al., 2008). Black arrows represent the mercury inputs from the Idrija mercury mine (Isonzo River) and the chlor-alkali plant (CAP) into the Lagoon. The dashed line indicates the administrative border of the two basins. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

2004; Point et al., 2007) and can give an estimation of the potential risk for Hg bioaccumulation in the biota, which can pose a threat to human health through seafood consumption (Sirot et al., 2008).

The biogeochemical cycling of Hg at the sediment–water interface in the eastern basin of the Lagoon was recently investigated by means of both an *in situ* and a laboratory incubated benthic chamber (Covelli et al., 2008). The authors measured substantial fluxes of MeHg from the sediment to the overlying water column, particularly under hypoxic conditions, which sometimes affect the shallow lagoon waters, characterized by infrequent water renewal. Thus, the Hg-contaminated Lagoon sediments (up to 13 $\mu g\ g^{-1}$ in the eastern basin) were identified as a potential threat to the aquatic trophic chain.

Given the level of contamination of the Marano and Grado Lagoon and the evidence of substantial fluxes of Hg and MeHg from the sediments, the multidisciplinary research project "MIRACLE" (Mercury Interdisciplinary Research for Appropriate Clam farming in a Lagoon Environment) was set up in 2008. The aim of the project was to identify which areas pose the least risk of Hg bioaccumulation for commercial Manila clams. To this purpose, Hg and MeHg content in *Tapes philippinarum* was monitored in natural and seeded populations (Giani et al., 2012).

As part of the MIRACLE project, the biogeochemical cycling of Hg at the sediment–water interface was studied by means of *in situ* benthic chambers. Fluxes of Hg species from bottom sediments into the water column were measured and it was evaluated if and where the mobility of Hg could be considered a threat to the extent that further monitoring activities should be recommended to the local authorities. *In situ* experiments were conducted in proximity of two of the clam seeding fields: one is distinctive of the typical environmental conditions of an area proposed for the extension of clam farming; the other was chosen because of its vicinity to an area forbidden to such activities, where Hg concentration in sediments, as well as speciation results (Piani et al., 2005) suggested that more mobile and potentially bioavailable Hg species could be present. Seasonal daily benthic fluxes, accumulation rates and burial of Hg in the sediment were combined to obtain a tentative annual budget for Hg at the experimental stations. Furthermore, evidence from this study was compared to previous research (Covelli et al., 2008) performed in the eastern sector of the Lagoon, in order to highlight differences in terms of Hg behavior in relation to the different characteristics of the investigated sites.

2. Study area

2.1. Environmental setting

The Marano and Grado Lagoon (Fig. 1), located along the Northern Adriatic coast between the Tagliamento and Isonzo River deltas, covers an area of about 160 km^2. It receives silty and clayey sediment from the two river deltas through the tidal inlets, as well as sandy material from erosion of the barrier islands (Brambati, 1970). The lagoon is characterized by semi-diurnal tidal fluxes (65–105 cm range). Salinity is very low close to the river mouths (2–7) but increases toward the tidal inlets (24–36) (Covelli et al., 2009). A deep navigable channel connects the Buso inlet with the Aussa–Corno river system, where industrial and port activities are located. The channel separates the Marano Lagoon to the west (84 km^2) from the Grado Lagoon to the east (76 km^2).

Freshwater inputs are mostly limited to the western sector and the overall average amount of freshwater discharge has been estimated at around 70–80 $m^3\ s^{-1}$, with a maximum peak of 100 $m^3\ s^{-1}$ (Mosetti, 1983). The main freshwater input comes from the Aussa–Corno river system which flows into the central sector of the lagoon. Whereas the Corno River has a limited freshwater discharge (5–8 $m^3\ s^{-1}$), the Aussa River is characterized by the presence of several tributaries, drainage channels and irrigation ditches, and its total discharge reaches 8–20 $m^3\ s^{-1}$ (Covelli et al., 2009).

2.2. Mercury in the Marano and Grado Lagoon

Mercury contamination in the Marano and Grado Lagoon has a double origin. The first is suspended matter from the Isonzo River, which drains the cinnabar (HgS)-rich deposits of Idrija (Slovenia), the world's second largest Hg mine after Almadèn (Spain). Although mining in Idrija stopped in 1995, large quantities of Hg still reach the nearby Gulf of Trieste (Horvat et al., 1999; Rajar et al., 2000; Covelli et al., 2006a) and enter the lagoon system when river discharge reaches its peak and specific wind conditions occur simultaneously (Covelli et al., 2007). The second source of contamination is a chlor-alkali plant, where metallic Hg was used as a catalyst for the electrolytic production of Cl_2. It has been estimated that a total of 186,000 kg of Hg were deliberately discharged into the Aussa–Corno river system (Piani et al., 2005) between 1949 and 1984. The distribution and speciation of Hg in bottom sediments of a limited sector (Buso basin) of the Marano and Grado Lagoon was investigated by Piani et al. (2005). The results showed that the highly insoluble HgS ($K_{sp} = 10^{-36.8}$; Ravichandran, 2004) dominates the central sector of the lagoon, while non-HgS compounds constitute up to 98% of total Hg in the Aussa–Corno River mouth and were found to be correlated to fine-grained material and organic matter. The authors concluded that the most worrying areas for potential Hg remobilization from sediments, and/or transformation into MeHg, were those affected by the influence of the freshwaters from the Aussa–Corno River, highlighting the role of this fluvial system as a "conveyor belt" of potentially bioavailable Hg compounds from the chlor-alkali plant to the river and the lagoon.

These findings raised questions about the mobility of Hg in these contaminated environments and the risk that they pose for the aquatic biota (Brambati, 2001). This is of great concern especially in the western basin (Marano Lagoon), where commercial clam farming of *Tapes philippinarum* is performed in limited, authorized areas, especially in the sandy sediments close to the Lignano Sabbiadoro sea inlet (Sfriso et al., 2008) and where other areas have been proposed for the extension of such activities.

3. Materials and methods

3.1. Benthic chamber experiments

The *in situ* benthic chamber experiments at sites MB and MC (Fig. 1) were carried out seasonally during three campaigns: October 2008, February/March 2009, and July 2009, corresponding to autumn, winter, and summer seasonal conditions, respectively. Two benthic chambers were simultaneously deployed for each experimental site. A dark benthic chamber was used in parallel with a light (transparent) one to evaluate the effect of solar radiation on biogeochemical processes and Hg cycling at the sediment–water interface.

The benthic chambers are square boxes with a base of 50 × 50 cm and a height of 29 cm. Detailed characteristics of the chambers are given in Covelli et al. (1999, 2008).

Samples were collected through a flexible polyethylene tube at about 2-h time intervals (from $t_0 = 0$ to $t_f = 8$ h). All water samples were filtered through 0.45 μm pore size Millipore Millex HA membrane filters, except for dissolved O_2.

3.2. Sediment core collection and handling

Short sediment cores were collected for pore-water extraction and analyses of both the solid and the liquid phase. Sediment cores were immediately transported to the laboratory and, after supernatant water collection, were extruded and sectioned into slices (0–1, 1–2, 2–3.5, 3.5–5 and 5–7 cm) in a N_2-filled chamber to preserve the original redox conditions. Pore waters were extracted by centrifugation at *in situ* temperature (3500 rpm; $t = 40$ min), filtered through membrane filters (0.45 μm pore size, Millipore Millex HA), collected and stored until analysis as reported in the specific reference methods. Solid-phase samples were freeze-dried (Scanvac, CoolSafe 55-4), homogenized with a mortar and pestle and sieved through a 420 μm screen to remove coarse shell debris before subsequent analysis.

3.3. Analyses

3.3.1. Solid phase

For grain-size analysis, an aliquot (15–20 g) of fresh sediment was treated with H_2O_2 (3%) for a minimum of 24 h, to eliminate most of the organic matter. Subsequently, the sediment was wet-sieved through a 2-mm sieve to remove coarse shelly fragments. The resulting <2 mm fraction was analyzed with a laser granulometer (Malvern Mastersizer, 2000).

Organic carbon (C_{org}) and nitrogen (N_{tot}) content in freeze-dried and homogenized sediment samples were determined using a Perkin Elmer 2400 CHN Elemental Analyzer, as reported in De Vittor et al. (2012).

Total Hg (THg) was determined after total digestion (HF and *aqua regia*), following EPA Method 3052, in a closed microwave system (Milestone, MLS 1200). Final determination was performed by CV-AAS (Perkin Elmer, AAnalyst 100-FIAS) after a pre-reduction step ($NaBH_4$ 3% in NaOH 1%). Results obtained were in good agreement with the certified value (3.04 ± 0.20 mg kg^{-1} Hg; PACS-2 Marine Sediment, NRCC) and the relative standard deviation of at least three determinations was <5%. The limit of detection was approximately 0.13 mg kg^{-1}.

Methylmercury was determined following the procedures detailed in Horvat et al. (1993a) and Liang et al. (1994a,b) after acid extraction and separation of the organic phase. Final determination was performed by GC-AFS (Brooks Rand Model III). Accuracy was determined with two CRMs (BCR 580 Estuarine Sediment and IAEA 433 Marine Sediment). The precision in CRMs was 3%, expressed as the relative standard deviation of at least three independent determinations. The limit of detection was approximately 50 pg MeHg g^{-1}.

3.3.2. Dissolved phase

Total Hg (THg) determination was conducted according to Horvat et al. (1991). Exposure of the sample to ultraviolet light was followed by oxidation with BrCl (0.5%). A pre-reduction step using $NH_2OH \cdot HCl$ (0.25 mL 30%) was followed by reduction with $SnCl_2$, gold trapping and the detection by CV-AFS (Brooks Rand, Model III). BCR 579 was used as a CRM. The reproducibility of the method was 4%, whereas the limit of detection was 0.2 ng L^{-1}.

Methylmercury (MeHg) was determined following the procedures detailed in Horvat et al. (1993b) and Liang et al. (1994a,b). MeHg was extracted by distillation. The detection step was the same as that mentioned for the solid phase. Recovery was estimated by spiking the samples with a known amount of MeHg prior to extraction and analysis. On average, the recovery was around 80%. The results in each batch were corrected for the recovery factor. The reproducibility, expressed in relative standard deviation, varied from 5% to 10%. The limit of detection was approximately 50 pg MeHg L^{-1}.

Dissolved gaseous Hg (DGM) was determined immediately after sampling by purging and collecting the volatile Hg species in a sampling gold trap, which was then transferred to a double amalgamation CV-AFS analyzer system (Tekran 2500) as described in detail by Horvat et al. (2003) and Gårdfeldt et al. (2003). The system was calibrated by gas phase Hg (Hg^0) kept at 4 °C (Tekran, model 2505 mercury vapor calibration unit). The repeatability of the method was 4% whereas the detection limit was 10 pg L^{-1}.

Total dissolved Fe and Mn were analyzed by GF-AAS (Perkin Elmer, AAnalyst 100) using $Mg(NO_3)_2$ as a matrix modifier. The detection limit for Fe and Mn was 0.01 μmol L^{-1}. H_2S was determined spectrophotometrically after trapping with Zn acetate, as reported in Grasshoff et al. (1983). Dissolved inorganic (DIC) and organic (DOC) carbon were determined as reported in De Vittor et al. (2012).

4. Results and discussion

4.1. Solid phase

Sediment grain size was quite similar at the two experimental sites and texturally uniform with depth, consisting mostly of clayey silt according to Shepard's classification (1954). The average THg content was 1.44 ± 0.24 μg g^{-1} at MB and 4.33 ± 0.24 μg g^{-1} at MC (Fig. 2). These values are up to one order of magnitude higher than the estimated natural background for the nearby Gulf of Trieste (0.13 ± 0.04 μg g^{-1}; Covelli et al., 2006b) and similar to those reported by Acquavita et al. (2012). MeHg at MC (1.70 ± 0.61 ng g^{-1}) was slightly higher than at MB (1.14 ± 0.14 ng g^{-1}) and the highest MeHg values were generally found in the top 1 cm, with the exception of the March 2009 campaign when a subsurface MeHg peak at the 5–7 cm depth level was found for MC (Fig. 2).

The MeHg/THg ratio at both stations ranged from 0.02% to 0.16%. Slightly higher values were reported by Bloom et al. (2004b) for the Venice Lagoon (0.05–0.30%), by Muresan et al. (2007) for the Thau Lagoon in France (0.02–0.80%), and by Covelli et al. (2008) for the Grado Lagoon (0.001–0.20%).

Sediments at MC appear to be richer in organic matter (C_{org} 1.05%; N_{tot} 0.14%) compared to MB (C_{org} 0.76%; N_{tot} 0.12%). This is probably due to higher levels of riverine inputs and possibly to the presence of several industrial activities along the Aussa–Corno river system. C_{org} and N_{tot} showed different behavior among the seasons. Peak values for both parameters moved downwards in the sediment during summer, suggesting an active degradation of the organic matter. The average C_{org}/N_{tot} ratios were fairly constant in autumn and winter (from 8 to 10) but decreased during summer (about 6) probably as a consequence of lower inputs of refractory organic matter, increased production of nitrogen-rich autochthonous organic compounds (Goñi et al., 2003) and enhanced remineralization of labile organic detritus (Hedges et al., 1997).

4.2. Pore-water chemistry

Seasonal variation in pore-water THg and MeHg concentrations is evident at both experimental sites (Fig. 3). The highest THg values were found during July 2009, where 675 ng L^{-1} were found at MB; this was the highest value recorded in this study. On the other hand, during the colder seasons, THg concentration was significantly lower and the highest values were found at MC (Table 1).

The highest pore-water Mn concentration (Fig. 3) at MB and MC was always located in the uppermost layer (0–1 cm) and the two stations showed similar vertical profiles, despite some differences in concentration ranges. Higher Mn concentrations appeared at MB (0.05–0.29 μM) and MC (0.1–0.16 μM) in winter, compared to autumn, suggesting the enhanced relative importance of Mn respiration in surface sediments during lower temperatures, microbial activity and increased oxygen penetration (Hines et al., 1997). In winter, the dissolved Mn and Fe zones in the surface layer at MC overlapped and some dissolved Mn may also have originated from the reduction of Mn by Fe^{3+} (Canfield et al., 1993). In autumn, the dissolved Mn peak was found lower into the sediment, due to higher microbial activity and infauna bioturbation maintaining a subsurface cycling of metals. The importance of Mn reduction in organic matter mineralization is also suggested by the pore-water DIC and DOC profiles, presented in De Vittor et al. (2012). The highest pore-water Fe concentration (Fig. 3) was found at the 1–2 cm deep layer in autumn and at the 2–3.5 cm deep layer in winter at both sampling sites, showing the location of Fe reduction below the Mn reduction zone.

Hg removal by the formation of Fe/Mn oxyhydroxides could be one of the factors controlling Hg partitioning between the solid and the dissolved phase (Gagnon et al., 1996; Bloom et al., 1999), but the lack of correlation between Fe/Mn and Hg pore-water concentration at both sites suggests that it is not the most important ($n = 20$, $r^2 = 0.10$, $p = 0.17$ for Fe/Hg; $n = 29$, $r^2 = 0.017$, $p = 0.51$ for Mn/Hg).

Pore-water data for H_2S was limited to the summer campaign (Fig. 3). Overall, H_2S concentration was very low (<2.5 μmol L^{-1}) and, on average, H_2S was slightly higher for MC than MB. However, no significant peaks were observed moving downcore, thus suggesting that no optimal zone for sulfate reduction activity was present.

MeHg was higher at MC compared to MB, except for the summer campaign. The highest concentration was found in the 5–7 depth layer at MC in October 2008 (6.5 ng L^{-1}). At both sites the methylation zone moves upwards in the sediment during summer, more markedly at MB. Similar results were reported for the Grado Lagoon by Covelli et al. (2008). The observed decoupling between THg and MeHg profiles (both at MB and MC) suggests that Hg availability is not the sole driver for methylation during summer. In fact, it is well known that several processes affect MeHg contents in pore waters, for instance, *in situ* production by methylating bacteria (Compeau and Bartha, 1985; Gilmour et al., 1992; Choi et al., 1994; Fleming et al., 2006; Kerin et al., 2006), dissolution of authigenic Fe and Mn oxyhydroxides (Gagnon et al., 1997; Bloom et al., 1999) and the quality and quantity of DOM in anoxic sediments (Gagnon et al., 1996; Lambertsson and Nilsson, 2006).

Compared to previous experiments conducted in the Grado Lagoon by Covelli et al. (2008), MeHg contribution to the dissolved phase seems to be of minor importance, suggesting that methylation processes in the Marano Lagoon could be less intense as a result of less favorable environmental conditions and an increase in MeHg degradation activity (Hines et al., 2012). However, it must be noted that THg content in sediments of the Grado Lagoon is generally higher than in the Marano sector (Acquavita et al., 2012), thus representing a greater potential reservoir for Hg transformation processes. Although sedimentary Hg in the Grado sector is thought to be mainly associated with cinnabar (HgS) detritus (Acquavita et al., 2012), which has poor solubility ($K_{sp} = 10^{-36.8}$), both dissolved sulfide (Benoit et al., 1999) and organic matter (Ravichandran, 2004; Slowey, 2010) can enhance HgS dissolution, thus leading to greater availability of dissolved Hg for methylation processes.

The partitioning of Hg species between the solid and the dissolved phase can be described in terms of the Log K_D value, where K_D is expressed in L kg^{-1} (Hammerschmidt et al., 2004). Log K_D values for THg (Table 1) were higher in autumn and winter (about 5 for MB and MC), while the lower values found in summer (3.57 for MB and 4.79 for MC) reflect the enhanced release of Hg into pore waters. The summer period is characterized by a greater consumption of OM, and it has already been reported (Marvin-DiPasquale et al., 2009) that decreasing OM content is coupled with lower K_D values. Hammerschmidt et al. (2004) suggested that organic ligands may affect the speciation of dissolved Hg complexes in anoxic low-sulfide sediments, despite evidence from chemical speciation models that show sulfide is the major ligand of both dissolved Hg(II) (Benoit et al., 1999) and MeHg (Dyrssen and Wedborg, 1991). Overall, Hg K_D values for MB and MC were lower than those reported by Covelli et al. (2008) for the Grado Lagoon and by Covelli et al. (1999) for the Gulf of Trieste, but similar to those reported by Hines et al. (2006) for the Isonzo River mouth.

Seasonal average Log K_D values for MeHg were rather uniform at MB (about 3), but increased at MC (from 2.84 in autumn to 4.11 in summer). These data suggest a substantial equilibrium between MeHg production and degradation at MB. At MC, the release of MeHg into pore waters seems to be favored in autumn, whereas in winter, and especially in summer, MeHg is preferentially bound to sediment particles. It must be noted that pore-water MeHg concentrations in autumn and winter at MC were particularly high in the 5–7 cm depth layer (Fig. 3). It is possible that the bioturbation of the upper layers of sediment prevented MeHg accumulation in the pore water.

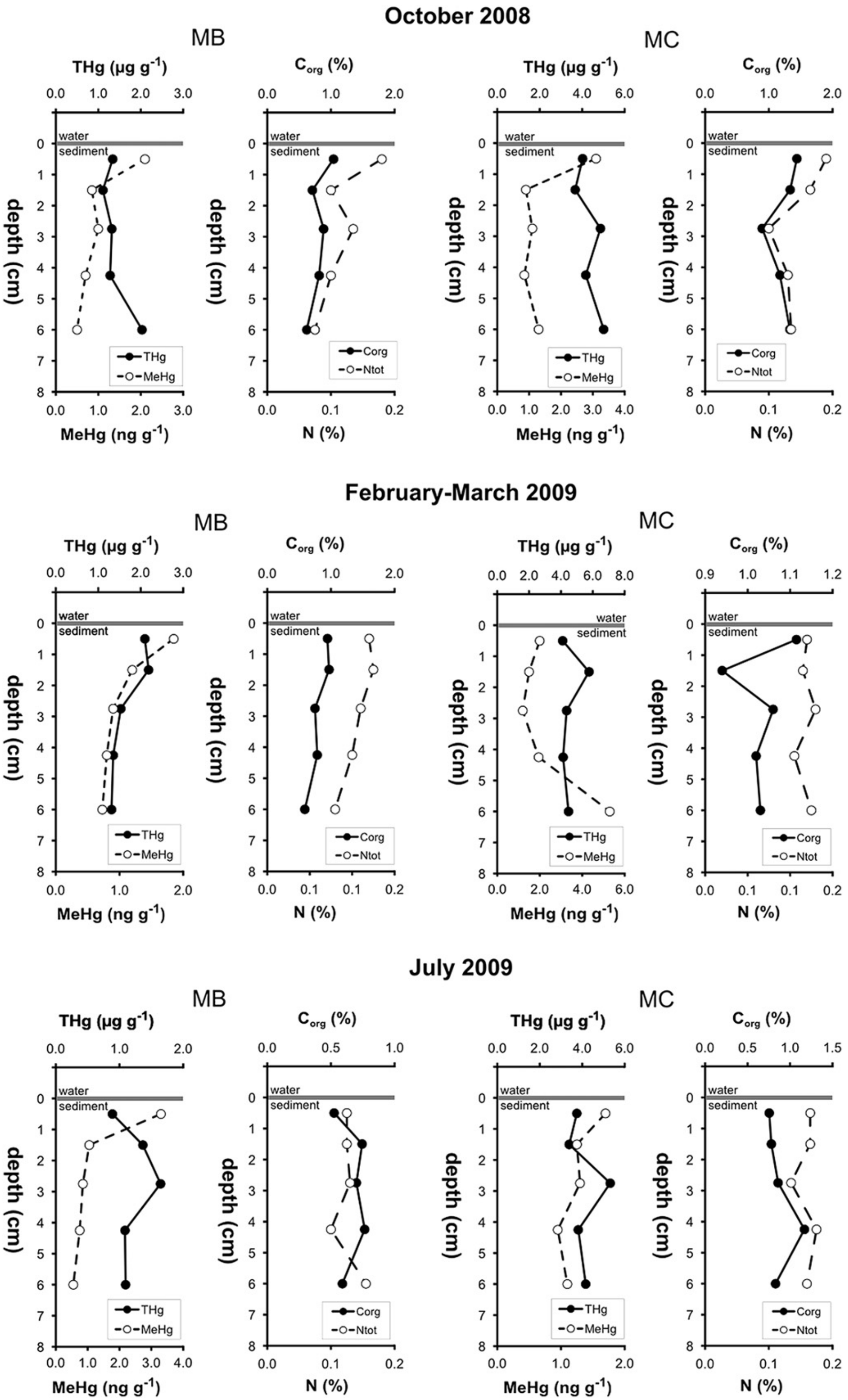

Fig. 2. Solid-phase seasonal vertical profiles for total Hg (THg), methyl-Hg (MeHg), organic carbon (C_{org}), and nitrogen (N_{tot}) at the MB and MC stations in the Marano Lagoon.

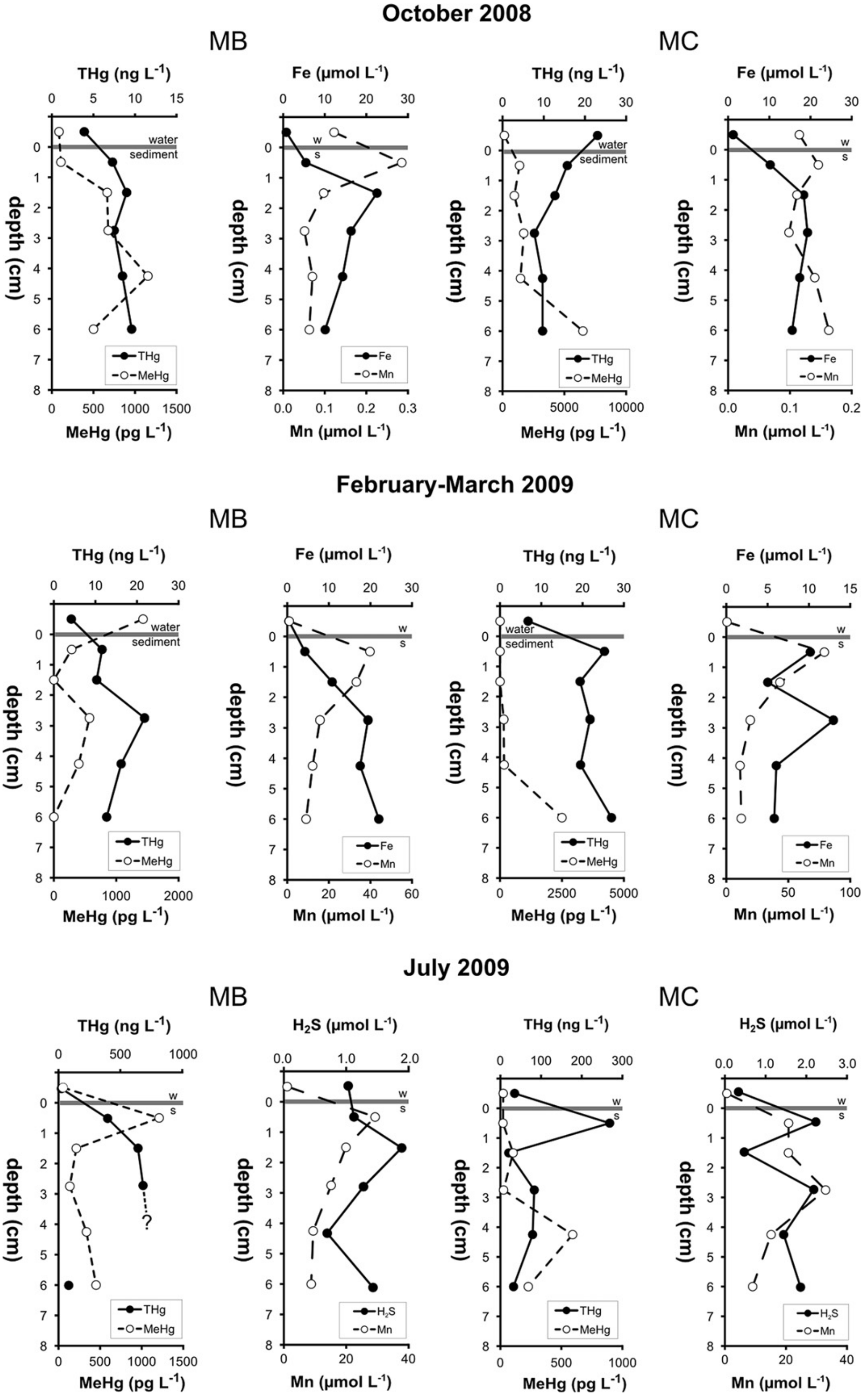

Fig. 3. Pore-water seasonal vertical profiles for total Hg (Hg), methyl-Hg (MeHg), Fe, Mn, and H_2S at the MB and MC stations in the Marano Lagoon.

Table 1
Seasonal average THg and MeHg content and partition (Log K_D) in sediments and pore waters of the Marano Lagoon.

Site	Period	Sediment			Pore water			Log K_D (L kg^{-1})	
		THg (μg g^{-1})	MeHg (ng g^{-1})	MeHg (%)	THg (ng L^{-1})	MeHg (pg L^{-1})	MeHg (%)	THg	MeHg
MB	Autumn	1.42	1.03	0.08	8.40	622	7.42	5.22	3.27
	Winter	1.70	1.10	0.06	14.5	418	2.88	5.07	3.44
	Summer	1.22	1.30	0.12	441	469	0.11	3.57	3.47
	Average	*1.45*	*1.14*	*0.09*	*155*	*503*	*3.47*	*4.62*	*3.39*
MC	Autumn	4.35	1.45	0.03	11.1	2397	21.6	5.60	2.84
	Winter	4.57	2.39	0.05	22.6	938	4.15	5.31	3.77
	Summer	4.09	1.26	0.03	96.9	195	0.20	4.79	4.11
	Average	*4.34*	*1.70*	*0.04*	*43.5*	*1177*	*8.65*	*5.23*	*3.57*

Considerable percentages of the MeHg/THg ratio in pore waters were found in October and March, while in July MeHg represented less than 0.5% of THg for both stations (Table 1). In Covelli et al. (2008) the MeHg/THg ratio ranged from 0.1 to 15%, considering all seasons, similar to values reported by Muresan et al. (2007) for the Thau Lagoon. Higher values were reported for the Gulf of Trieste (Covelli et al., 1999), where subsurface maxima were up to 58%, during autumn.

4.3. Diffusive benthic fluxes

Diffusive fluxes represent an instantaneous measure of the flux of solutes diffusing from sediment pore water to the overlying water column, along a concentration gradient. In the present study, diffusive benthic fluxes were determined by application of Fick's first law, using diffusion coefficients from Gobeil and Cossa (1993) and Mason et al. (1993) for THg and from Hammerschmidt et al. (2004) for MeHg, as previously reported in Covelli et al. (2008).

In the absence of bioirrigation, Fick's first law can be expressed as:

$$F = -\left(\frac{\Phi D_W}{\theta^2}\right)\frac{\partial C}{\partial x}$$

where F is the flux of a solute with concentration C at depth x, Φ the sediment porosity, θ the tortuosity (dimensionless) and D_W is the diffusion coefficient of the solute in water in the absence of the sediment matrix.

Tortuosity was estimated from porosity, following Boudreau (1996):

$$\theta = \sqrt{1 - \ln\left(\Phi^2\right)}$$

THg fluxes were similar in MB and MC, except for an influx in the October campaign at MC, and the highest values were associated with the summer campaign (Table 2), most probably as a consequence of more intense benthic metabolism in the surface sediment, driven by higher temperatures.

MeHg fluxes were rather different between the two stations (Table 2). There was no evident relationship between MeHg diffusion and temperature for MC, while for MB higher fluxes were associated with higher temperatures. Overall, MeHg fluxes appeared to be of modest intensity compared to the high concentration of MeHg in pore waters.

Lower THg fluxes were reported by Covelli et al. (2008) for the Grado Lagoon (site BAR), where the highest flux was also measured in the summer, but it only accounted for 95 ng m^{-2} d^{-1}, which is about five times lower than diffusive fluxes in the Marano sector (Table 2). Conversely, MeHg fluxes were generally higher in the Grado Lagoon and the highest flux (16.3 ng m^{-2} d^{-1}) was measured in autumn.

4.4. Benthic chamber experiments

Considering all seasons, THg showed little daily variation in concentration with time at both stations, while MeHg and DGM showed significant daily and seasonal fluctuations (Figs. 4–7). In order to verify that the average concentration of Hg species in the benthic chambers (Table 3) varied significantly with the season, the Kruskal–Wallis non-parametric test was applied ($n = 15$).

Table 2
Seasonal diffusive and daily *in situ* benthic fluxes for the Marano (MB, MC) and Grado (ART, BAR; Covelli et al., 2008) Lagoon sites. For diffusive fluxes positive values are indicative of an efflux, while negative values represent an influx or scavenging from the water column.

Site	Period	T (°C)	Diffusive fluxes (ng m^{-2} d^{-1})		*In situ* benthic fluxes (ng m^{-2} d^{-1})					
			THg	MeHg	Light chamber			Dark chamber		
					THg	MeHg	DGM	THg	MeHg	DGM
MB	Autumn (October 2008)	18.5	6.8	0.1	2354	83.9	49.9	5355	240.2	78.3
	Winter (February–March 2009)	8.8	14.8	−5.5	11,163	145.9	109.8	5622	189.6	165.2
	Summer (July 2009)	24.0	570	4.2	4933	90.6	48.5	2882	145.0	134.4
MC	Autumn (October 2008)	18.0	−12.2	4.9	2843	120.2	24.0	5168	130.8	48.5
	Winter (February–March 2009)	11.9	31.7	nd	2796	184.3	176.7	7805	138.0	206.6
	Summer (July 2009)	26.9	413	0.0	4136	178.2	1552.5	2810	88.7	302.4
ART	Autumn (October 2003)	21.0	nd	17	14,920	1020	1950			
	Winter (February 2004)	5.0	112	3	6890	90	780			
	Summer (June 2003)	28.0	nd	nd	41,080	2290	nd			
BAR	Autumn (October 2003)	21.0	nd	17	5900	700	320			
	Winter (February 2004)	5.0	−37	4	7660	210	1120			
	Summer (June 2003)	28.0	95[a]	−2[a]	33,200	1490	nd			

[a] Summer diffusive fluxes for THg and MeHg in BAR refer to July 2005. All data for ART and BAR adapted from Covelli et al. (2008).

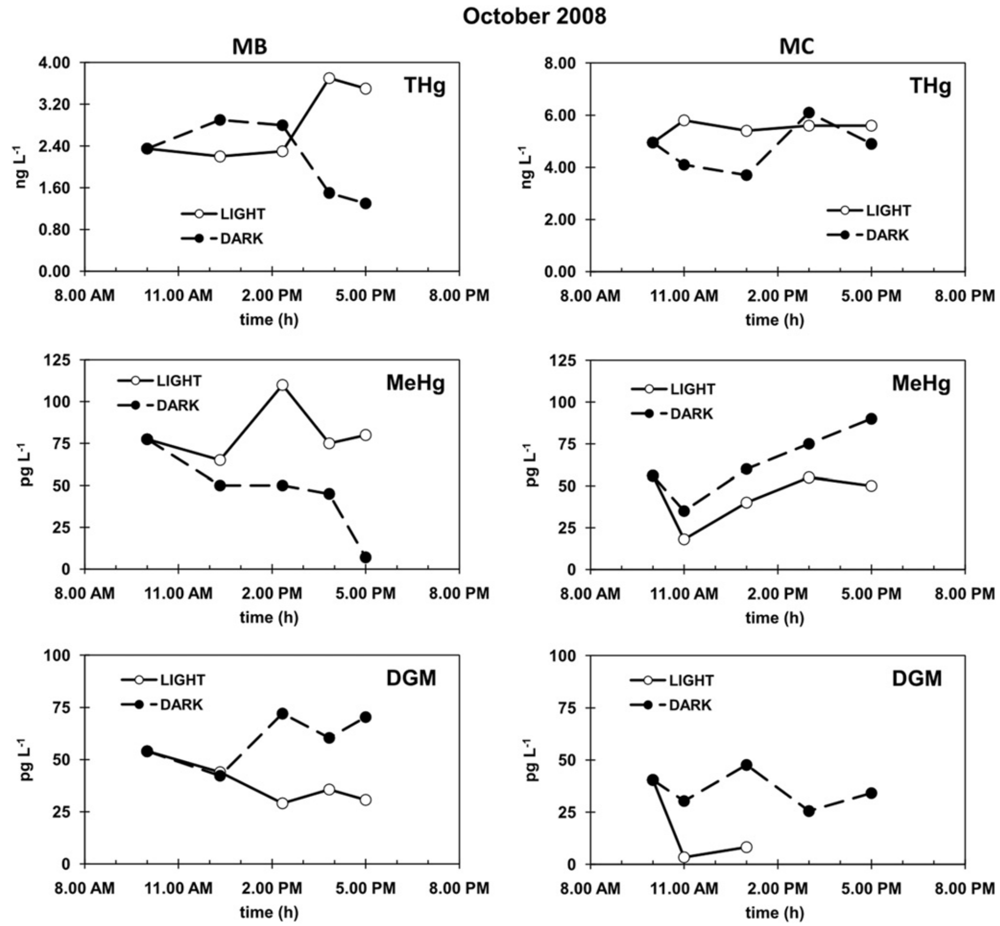

Fig. 4. Concentration of total Hg (THg), methyl-Hg (MeHg), and dissolved gaseous Hg (DGM) inside the light and dark benthic chambers during the *in situ* autumn campaign at the MB and MC stations in the Marano Lagoon (October 2008).

Statistical results were considered significant at a level of $p < 0.05$. Seasonal variation of MeHg and DGM at MC was significant for both chambers ($p < 0.01$), while THg reported a significant p value ($p = 0.01$) only for the light chamber. At MB, variation with the season was significant for THg in both chambers and for MeHg in the light chamber ($p = 0.02$). Overall, the average THg, MeHg and DGM concentrations detected in the benthic chambers were consistently higher at MC compared to MB and the highest MeHg and DGM values were found during summer (Table 3).

During the summer campaign (Fig. 6), a longer experiment (21 h) was performed at MC with the aim of monitoring benthic dynamics in the light chamber throughout the night. DGM displayed unexpectedly high and increasing concentrations, up to 1 ng L^{-1} at the end of the experiment. In comparison, both the average concentration registered in the light chamber at MB (63.2 pg L^{-1}) and in the dark chamber at MC (300 pg L^{-1}) were lower by 1–2 orders of magnitude.

Several authors (e.g. Kim and Fitzgerald, 1988; Amyot et al., 1997a,b; Rolfhus and Fitzgerald, 2001; Andersson et al., 2007, 2011) suggest that DGM production in the aquatic environment is mainly driven by photochemical reactions. However, there is growing evidence (Monperrus et al., 2007; Fantozzi et al., 2009) that this process can also occur in the dark, involving an active role for bacteria, as previously observed by Kim and Fitzgerald (1986, 1988) and Rolfhus and Fitzgerald (2004).

Fantozzi et al. (2009) pointed out that, while photochemical reduction only occurs during the day, DGM production by bacteria occurs both in light and dark conditions. Moreover, the limiting factor in DGM production is related to the amount of Hg(II) available for reduction, rather than the total bacterial charge. In the present experiments, the amount of THg suggests that it was not a limiting factor.

In order to rule out an eventual light leakage in the dark chamber, the intensity of solar radiation in the photosynthetically active radiation (PAR) region ($\lambda = 400–700$ nm) was measured inside both chambers. The results were 3155 and 581 $\mu E\ m^{-2}\ s^{-1}$ for the light and dark benthic chamber, respectively. Thus, although there is apparently some infiltration of light in the dark chamber, there is a substantial difference in the amount of penetrating light. However, it should be noted that PAR measurements exclude ultraviolet (UV) radiation ($\lambda = 10–400$ nm), which is responsible for photochemical processes. Both chambers are made of polymethylmethacrylate (PMMA), which transmits up to 92% of visible light but filters UV light at $\lambda < 300$ nm. As a consequence, the light benthic chamber is transparent to UVA but blocks UVB and UVC. From seawater incubation experiments, Amyot et al. (1997a,b) reported that the relative contribution of visible, UVA, and UVB radiation to total DGM production was 46%, 31%, and 23%, respectively. Thus, the observed DGM production in the light chamber could be underestimated by approximately 25%.

DGM and MeHg measurements were also performed outside the benthic chambers in the autumn and summer campaigns (Fig. 7). During autumn, MeHg and DGM proceeded almost in parallel. MeHg was higher at MB (avg. 70.2 pg L^{-1}) than at MC (avg. 52.5 pg L^{-1}), and at both sites it peaked early in the afternoon. DGM was almost threefold higher at MC (avg. 206.9 pg L^{-1}) compared to MB (avg.

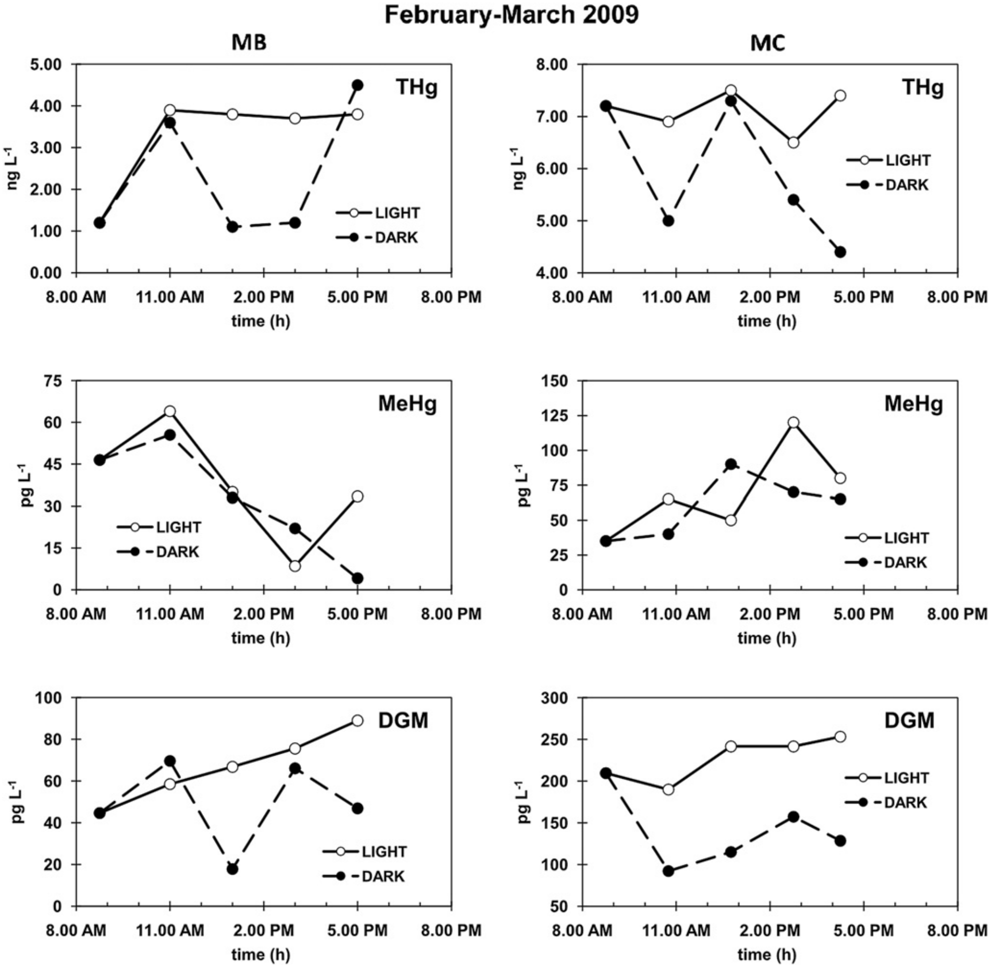

Fig. 5. Concentration of total Hg (THg), methyl-Hg (MeHg), and dissolved gaseous Hg (DGM) inside the light and dark benthic chambers during the *in situ* winter campaign at the MB and MC stations in the Marano Lagoon (February–March 2009).

68 pg L^{-1}), showing peaks in the central hours of the day. The DGM trend in the water column suggests a strong light dependence of Hg reduction processes, more evident than in the benthic chambers.

In summer, monitoring outside the chambers at MC lasted 21 h (Fig. 7). Interestingly, while MeHg showed a decrease in concentration during the night (from 120 pg L^{-1} to 38 pg L^{-1}), with a final surge after sunrise (96.5 pg L^{-1}), DGM peaked at 1 ng L^{-1} under dark conditions. An increase in DGM concentration during the night was already observed inside the light benthic chamber at MC (Fig. 6) but no decrease in concentration was detected. It is possible that the high DGM values found in the benthic chamber could have been due to DGM accumulation in the absence of degradation processes and/or lack of mixing and dilution by the water column.

The observed trends of MeHg and DGM under dark conditions suggest a possible relationship between the decrease in MeHg concentration and the increase in DGM in the water column, as also seen in October 2008 at MB. Clearly, under dark incubation conditions, only light-independent Hg transformation processes can occur. Monperrus et al. (2007) investigated Hg transformation processes in lagoon and marine waters of the Mediterranean Sea. In the deep euphotic marine layer, where light penetration is largely attenuated (only 0.1–1% of PAR), biologically mediated processes determine the fate of Hg(II), which acts as a common substrate for the formation of both MeHg and DGM through methylation and/or reduction processes.

In the Marano and Grado Lagoon, reductive demethylation could directly produce Hg(0), while a dark oxidative degradation of MeHg could yield Hg(II) substrate for the prompt formation of DGM (Baldi et al., 2012; Hines et al., 2012). Both mechanisms could remove fresh substrate for further methylation processes, resulting in a net increase of DGM in the water column and a decrease in the organic form. In this way, MeHg fluxing from the sediment to the water column could be lost to the atmosphere once demethylated and in gaseous form, thus mitigating the risk for MeHg accumulation in biota.

The behavior of MeHg and DGM during winter at MB (light chamber) further suggests a connection between MeHg degradation and DGM formation. However, in this case, photochemical processes could explain the degradation of MeHg and the reduction of Hg(II) to DGM, as already observed by several authors (Monperrus et al., 2007; Andersson et al., 2011 and references therein).

4.5. *In situ benthic fluxes*

To quantify THg, MeHg, and DGM mobility across the sediment–water interface, diurnal fluxes were calculated by integrating the area under the “concentration vs time” curve over an 8 h period and normalizing the results to 24 h (Covelli et al., 2008).

Benthic flux calculations are presented in Table 2 and compared to a similar investigation previously conducted in the Grado Lagoon (Covelli et al., 2008), where daily *in situ* benthic fluxes were calculated for sites BAR and ART (inside a fish farm) during three seasonal campaigns. MeHg fluxes for the light chamber were higher at MC than at MB for all three campaigns. DGM was also

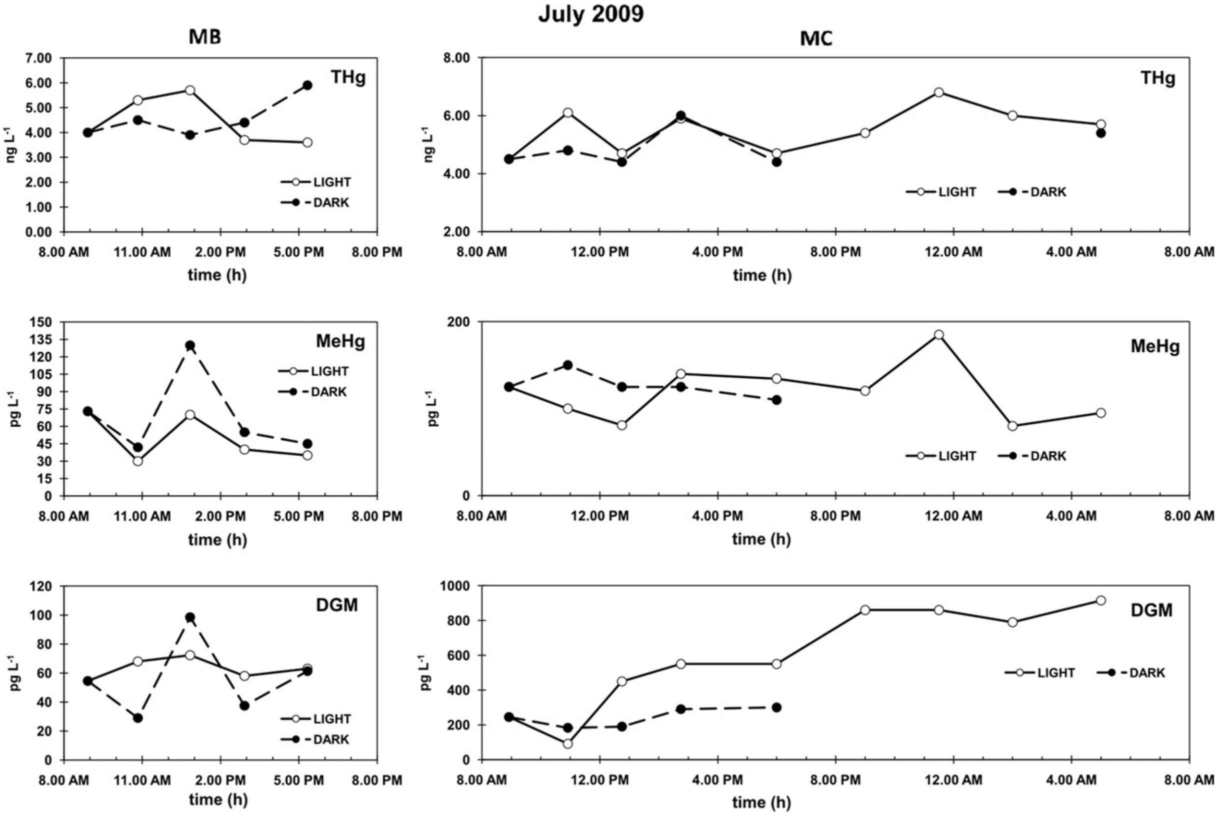

Fig. 6. Concentration of total Hg (THg), methyl-Hg (MeHg), and dissolved gaseous Hg (DGM) inside the light and dark benthic chambers during the *in situ* summer campaign at the MB and MC stations in the Marano Lagoon (July 2009).

higher at MC, with the exception of the autumn campaign. Notably, the DGM flux for MC in July accounted for around 1.6 μg m^{-2} d^{-1}, which is up to 30 times higher than at MB. On the contrary, THg fluxes were somewhat similar at the two stations, except for March 2009 when the calculated flux for MB (11.2 μg m^{-2} d^{-1}) was almost four times higher than at MC (2.8 μg m^{-2} d^{-1}).

In the dark chamber, THg fluxes were similar at the two sites in autumn and summer. In winter, a higher flux was measured at MC (7.8 μg m^{-2} d^{-1}) compared to MB (5.6 μg m^{-2} d^{-1}). MeHg fluxes were always higher at MB than at MC. A higher flux of DGM was detected in autumn at MB (78.3 ng m^{-2} d^{-1}), while higher fluxes were measured at MC during winter and summer (206.6 and 302.4 ng m^{-2} d^{-1}, respectively).

Overall, in the presence of light, MC releases MeHg and DGM more actively than MB. In the absence of light, MeHg fluxes are higher at MB than at MC, whereas DGM fluxes are higher at MC. THg behavior appears to be similar at the two sites, with the exception of winter.

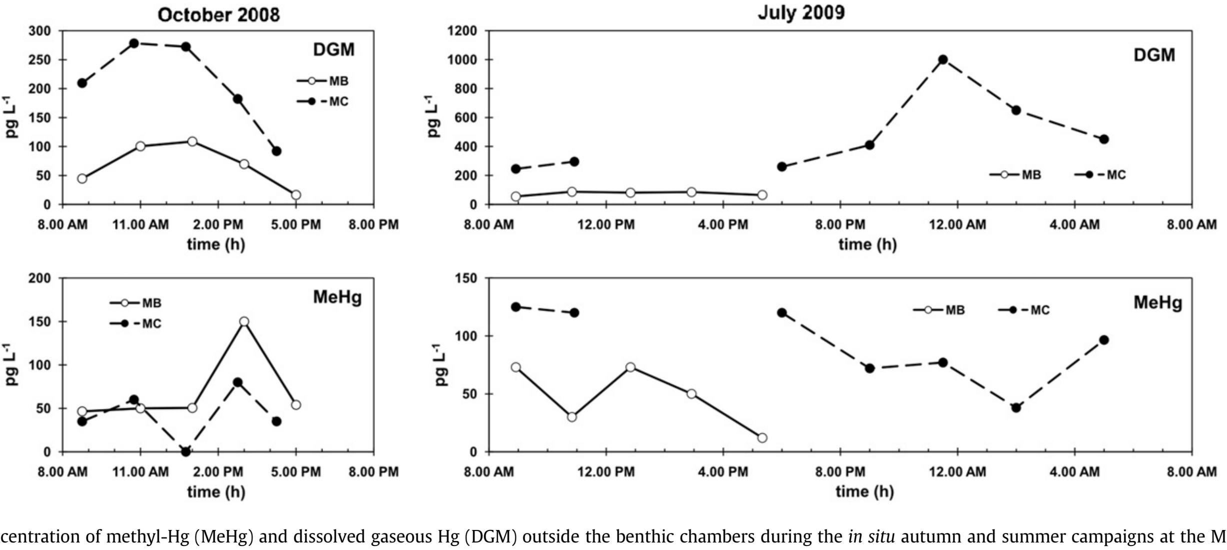

Fig. 7. Concentration of methyl-Hg (MeHg) and dissolved gaseous Hg (DGM) outside the benthic chambers during the *in situ* autumn and summer campaigns at the MB and MC stations in the Marano Lagoon (October 2008 and July 2009).

Table 3
Seasonal average concentration for THg, MeHg and DGM for sites MB and MC in the Marano and Grado Lagoon. DGM concentrations correspond to the sum of elemental Hg and dimethyl-Hg.

Site	Period	*T* (°C)	Light chamber			Dark chamber		
			THg (ng L^{-1})	MeHg (pg L^{-1})	DGM (pg L^{-1})	THg (ng L^{-1})	MeHg (pg L^{-1})	DGM (pg L^{-1})
MB	Autumn	18.5	2.81	81.5	38.6	2.17	45.9	59.8
	Winter	8.8	3.28	37.5	66.9	2.32	32.2	49.0
	Summer	24.0	4.46	49.6	63.2	4.54	69.0	56.2
	Average		*3.52*	*56.2*	*56.2*	*3.01*	*49.0*	*55.0*
MC	Autumn	18.0	5.47	43.8	17.3	4.75	63.2	35.6
	Winter	11.9	7.10	70.0	227.2	5.86	60.0	140.5
	Summer	26.9	5.53	123.0	795.0	4.92	127.0	241.6
	Average		*6.03*	*78.9*	*346.5*	*5.18*	*83.4*	*139.2*

The difference in MeHg and DGM fluxes between the two stations can be the result of both sediment characteristics and biogeochemical processes happening in the sediment as much as in the water column, where light can play an important role in determining their fate. No marked difference in methylation/demethylation transformation rate constants (Hines et al., 2012) and bacterial community (Baldi et al., 2012) was found between the two sites. The only notable difference between the two stations is the total Hg content in the sediment, which is almost threefold in MC compared to MB. However, total Hg content is not a good predictor of MeHg fluxes at the sediment–water interface. A speciation technique was applied to the surficial (0–1 cm) sediment of MB and MC (Acquavita et al., 2012) and the results showed that non-cinnabar compounds prevail at both stations (87%). However, according to the corresponding total Hg concentrations, the pool of Hg easily available for mobilization (non-cinnabar compounds) is larger in MC. Therefore, only a more detailed characterization of Hg speciation in the sediment using a selective sequential extraction could clarify which fractions make up for the non-cinnabar Hg compounds and would highlight if these fractions are present in different percentages at the two experimental stations.

If compared to the Marano sites, fluxes in the Grado Lagoon were consistently higher (Table 2). The highest fluxes of MeHg were measured during summer, whereas THg was also recycled more efficiently. In fact, the summer fluxes at BAR and ART were about one order of magnitude higher than in the Marano Lagoon. DGM fluxes were also higher in the Grado Lagoon, reaching almost 2 μg m^{-2} d^{-1} during autumn at the fish farm site.

The higher THg content in the Grado Lagoon sediments represents a greater potential reservoir for Hg transformation processes, with higher fluxes and a pattern suggesting an important role for temperature and organic matter degradation in enhancing Hg/MeHg release and production. The latter assumption is supported by the high concentration of nutrients and organic matter (DIC, DOC) found in the pore waters of the fish farming site ART by De Vittor et al. (2012) which is indicative of high metabolic activity.

4.6. Annual mercury budget

Seasonal daily benthic fluxes, accumulation rates (Covelli et al., 2012) and burial of Hg in sediments were combined to obtain a tentative annual Hg budget for the two experimental stations in the Marano Lagoon. A similar approach was proposed for the Grado Lagoon in Covelli et al. (2008) and the results are presented in Fig. 8. The estimated annual benthic fluxes are the result of a weighted average, considering October, February–March, and July daily fluxes as representative of 5.5, 4, and 2.5 months, respectively, on the basis of the average monthly bottom water temperature.

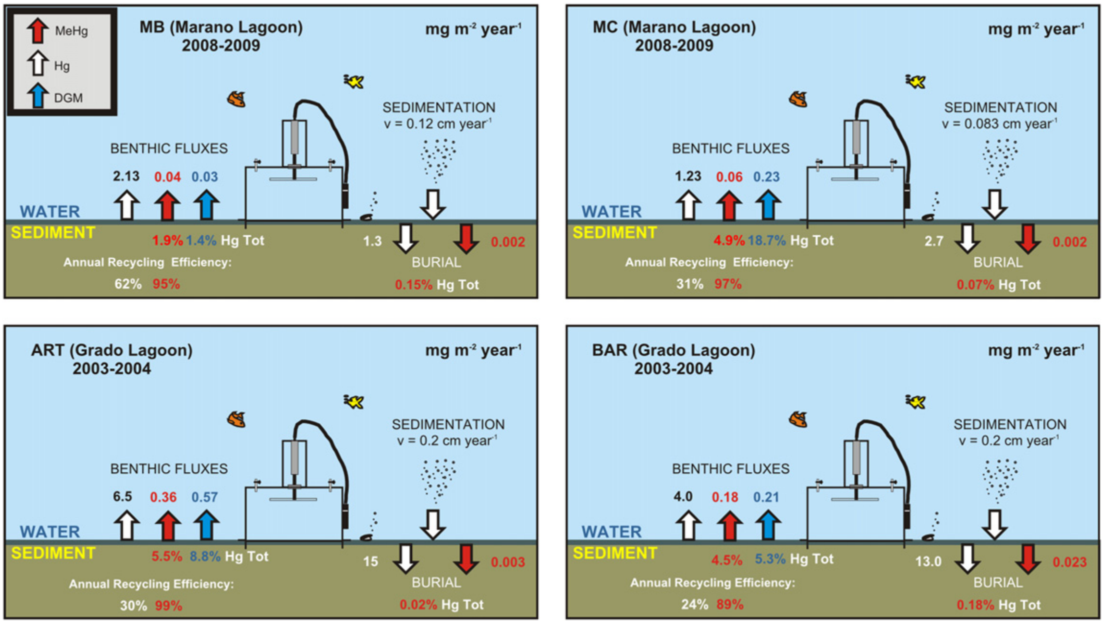

Fig. 8. Mercury budget in the Marano and Grado Lagoon (data for Grado Lagoon from Covelli et al., 2008).

The estimated total Hg annual benthic flux at MB was almost double that at MC. While the MeHg flux is similar at the two sites, it represents a higher percentage of the total Hg released from the sediment at MC compared to MB. The flux of DGM at MC prevails over the MeHg flux and is up to one order of magnitude higher than the relative DGM flux at MB. Thus, while MB releases a higher quantity of Hg from the sediment, methylation (4.9% of THg) and reduction (18.7% of THg) processes appear to be more intense at MC (Fig. 8).

Higher fluxes were estimated for the Grado Lagoon. The total Hg flux for both BAR and ART was from 2 to 3 fold higher than in the Marano Lagoon. MeHg, also, showed the same behavior and accounted for 4.5% and 5.5% of THg at BAR and ART, respectively. As a whole, DGM fluxes were higher in the Grado basin. At the fish farming site, DGM represented almost 9% of the total Hg annually released from the sediment and, at both stations, DGM fluxes were higher than MeHg fluxes.

The mean annual recycling efficiency (E) of THg (and, similarly, MeHg), can be assessed according to the following equation:

$$E = \frac{[\mathrm{Hg}]_{\mathrm{flux}}}{[\mathrm{Hg}]_{\mathrm{flux}} + [\mathrm{Hg}]_{\mathrm{burial}}}$$

where $[\mathrm{Hg}]_{\mathrm{flux}}$ is the loss of THg (MeHg) in the water column and $[\mathrm{Hg}]_{\mathrm{burial}}$ is the amount of THg (MeHg) buried in surface sediments. Burial was calculated from the sedimentation rate (ω), taking into account the concentration of sedimentary THg (MeHg) in the first centimeter (Gill et al., 1999), using the following equation:

$$[\mathrm{Hg}]_{\mathrm{burial}} = \omega[\mathrm{Hg}]\rho_{\mathrm{s}}(1 - \phi)$$

where ρ is the density (2.67 g cm^{-3}) and ϕ is porosity (from 0.703 to 0.797).

On the basis of radioisotope measurements with ^{210}Pb (Covelli et al., 2012), the sedimentation rate (ω) was estimated to be 0.12 cm y^{-1} at MB and 0.083 cm y^{-1} at MC. Thus, the amount of THg buried in the surface sediments accounts for approximately 1.3 mg m^{-2} y^{-1} at MB and 2.7 mg m^{-2} y^{-1} at MC. MeHg burial is calculated to be 0.15% of THg at MB, corresponding to 0.002 mg m^{-2} y^{-1}, and 0.07% at MC (0.002 mg m^{-2} y^{-1}).

From these calculations, it appears that similar, elevated percentages of MeHg (89–99%) are recycled annually at the experimental stations of both the Grado and the Marano basins and only a small percentage (0.02–0.18%) is buried in the sediment (Fig. 8). It is also evident that similar percentages of Hg (around 30%) are recycled annually to the water column at the Grado stations and at the MC site, while this percentage doubles at MB, reaching about 62%. However, it must be noted that since the annual budget is based on results from only three seasonal daily experiments, the degree of uncertainty over the possible under/overestimation of the results, due to such a scaling up, is currently unknown. Thus, such results should be considered as indicative of the different behavior of the considered stations in the Lagoon, with regards to Hg cycling, and not as a proper mass balance on the whole basin.

4.7. Significance of Hg mobility for rearing activities in the Marano and Grado Lagoon

Taking into account the estimated annual budget in the Marano and Grado Lagoon, sites in the Grado basin and in particular the fish farming site ART, appear to be more active both in terms of remobilization and transformation of Hg at the sediment–water interface. Thus, sediments of the Grado Lagoon can be considered as the most critical for Hg transfer from the sediment to the water column.

Although *Tapes philippinarum* can assimilate pollutants directly from the sediment or by its filter-feeding activity, the relationship between the metal concentration in the surface sediments and in the clam soft tissues is not always clear (Sfriso et al., 2008). At a Marano experimental station near the Lignano inlet, Sfriso et al. (2008) found no significant correlations between the Hg content in sediments, suspended particulate matter and clams. However, results from the present study highlight a possible link between Hg fluxes at the sediment–water interface and Hg accumulation in benthic organisms. In fact, Giani et al. (2012) reported significantly higher THg and MeHg contents in wild clam populations collected near the MC and BAR experimental stations, where the highest benthic fluxes were measured. Such results suggest that the western sector of the Lagoon (site MB) can be considered a more favorable area for clam farming over the eastern basin.

5. Conclusions

Mercury release in the Marano and Grado Lagoon is driven by several factors, including total Hg content, organic matter remineralization efficiency, microbial activity, partitioning of Hg between the solid and the dissolved phases and its interactions with dissolved sulphides and organic matter.

Benthic flux calculations suggest that Hg recycling at the sediment–water interface in the Marano Lagoon is not particularly intense. For both experimental sites the highest fluxes are generally present in the summer, when bacterial degradation of organic matter releases greater quantities of Hg into pore waters. The bioavailable fraction of pore-water Hg can subsequently be methylated, leading to higher MeHg fluxes in the summer, as already observed for the Grado Lagoon (Covelli et al., 2008). MeHg release is higher in sediments at the MC station, which is characterized by Hg of industrial origin, due to proximity to the Aussa–Corno River mouth, where chlor-alkali Hg discharges are known to have occurred. However, greater MeHg fluxes, by up to three orders of magnitude, have previously been reported for the Grado Lagoon (Covelli et al., 2008), where the total Hg content in the sediment is higher than in the Marano Lagoon and Hg methylation seems to be favored, despite its origin mainly being associated with the insoluble cinnabar (HgS) detritus flowing in from the Isonzo River.

For both experimental sites, Hg reduction, which drives the formation of DGM, seems to be the dominant transformation process in the water column, prevailing over methylation. This could be an important pathway for the natural Hg detoxification of lagoon waters. Moreover, DGM production in the dark was also found and justified by taking into account light-independent Hg reduction processes, probably due to the presence of Hg-resistant bacteria (Baldi et al., 2012; Hines et al., 2012).

Finally, on the basis of the estimated Hg and MeHg annual fluxes, which are also supported by evidence from bioaccumulation experiments (Giani et al., 2012), the western sector of the Lagoon seems to be the most suitable for the extension of rearing activities. However, given the complexity of both the lagoon ecosystem and the Hg biogeochemical cycle, investigations on sediment biogeochemistry should be promoted and carried out whenever a new clam rearing area is planned.

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References

Acquavita, A., Covelli, S., Emili, A., Berto, D., Faganeli, J., Giani, M., Horvat, M., Koron, N., Rampazzo, F., 2012. Mercury in the sediments of the Marano and Grado Lagoon (Northern Adriatic Sea): sources, distribution and speciation. Estuarine, Coastal and Shelf Science 113, 20–31.

Amyot, M., Mierle, G., Lean, D.R.S., McQueen, D.J., 1997a. Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes. Geochimica et Cosmochimica Acta 61 (5), 975–987.

Amyot, M., Gill, G.A., Morel, F.M.M., 1997b. Production and loss of dissolved gaseous mercury in coastal seawater. Environmental Science & Technology 31 (12), 3606–3611.

Andersson, M.E., Gårdfeldt, K., Wängberg, I., Sprovieri, F., Pirrone, N., Lindqvist, O., 2007. Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea. Marine Chemistry 104, 214–226.

Andersson, M.E., Sommar, J., Gårdfeldt, K., Jutterström, S., 2011. Air–sea exchange of volatile mercury in the North Atlantic Ocean. Marine Chemistry 125, 1–7.

Baldi, F., Gallo, M., Marchetto, D., Fani, R., Maida, I., Horvat, M., Fajon, V., Zizek, S., Hines, M., 2012. Seasonal mercury transformation and superficial sediment detoxification by bacteria of Marano and Grado Lagoon. Estuarine, Coastal and Shelf Science 113, 105–115.

Benoit, J.M., Gilmour, C.C., Mason, R.P., Heyes, A., 1999. Sulfide controls on mercury speciation and the bioavailability in sediment pore waters. Environmental Science & Technology 33, 951–957.

Bloom, N.S., Gill, G.A., Cappellino, S., Dobbs, C., Mc Shea, L., Driscoll, C., Mason, R., Rudd, J., 1999. Speciation and cycling of mercury in Lavaca bay, Texas, sediments. Environmental Science & Technology 33, 7–13.

Bloom, N.S., Moretto, L.M., Ugo, P., 2004a. A comparison of the speciation and fate of mercury in two contaminated coastal marine ecosystems: the Venice Lagoon (Italy) and Lavaca Bay (Texas). Limnology and Oceanography 49, 367–375.

Bloom, N.S., Moretto, L.M., Scopece, P., Ugo, P., 2004b. Seasonal cycling of mercury and monomethyl mercury in the Venice Lagoon (Italy). Marine Chemistry 91, 85–99.

Boudreau, B.P., 1996. The diffusive tortuosity of fine-grained unlithified sediments. Geochimica et Cosmochimica Acta 60, 3139–3142.

Brambati, A., 1970. Provenienza, trasporto e accumulo dei sedimenti recenti nelle lagune di Marano e di Grado e nei litorali tra i fiumi Isonzo e Tagliamento. Bollettino Della Società Geologica Italiana 9, 281–329.

Brambati, A., 2001. Coastal sediments and biota as indicators of Hg contamination in the Marano and Grado Lagoons. RMZ – Materials & Geoenvironment 48, 165–171.

Canfield, D.E., Thamdrup, B., Hansen, J.W., 1993. The anaerobic degradation of organic matter in Danish coastal sediments: iron reduction, manganese reduction, and sulfate reduction. Geochimica et Cosmochimica Acta 57, 3867–3883.

Choe, K.-Y., Gill, G.A., Lehman, R.D., Han, S., Heim, W.A., Coale, K.H., 2004. Sediment–water exchange of total mercury and monomethyl mercury in the San Francisco Bay–Delta. Limnology and Oceanography 49, 1512–1527.

Choi, S.-C., Chase Jr., T., Bartha, R., 1994. Enzymatic catalysis of mercury methylation by *Desulfovibrio desulfuricans* LS. Applied and Environmental Microbiology 60, 1342–1346.

Compeau, G.C., Bartha, R., 1985. Sulfate-reducing bacteria: principal methylators of mercury in anoxic estuarine sediment. Applied and Environmental Microbiology 50, 498–502.

Covelli, S., Faganeli, J., Horvat, M., Brambati, A., 1999. Porewater distribution and benthic flux measurements of mercury and methylmercury in the Gulf of Trieste (Northern Adriatic Sea). Estuarine, Coastal and Shelf Science 48, 415–428.

Covelli, S., Piani, R., Kotnik, J., Horvat, M., Faganeli, J., Brambati, A., 2006a. Behaviour of Hg species in a microtidal deltaic system: the Isonzo River mouth (northern Adriatic Sea). The Science of the Total Environment 368, 210–223.

Covelli, S., Fontolan, G., Faganeli, J., Ogrinc, N., 2006b. Anthropogenic markers in the Holocene stratigraphic sequence of the Gulf of Trieste (Northern Adriatic Sea). Marine Geology 230, 29–51.

Covelli, S., Piani, R., Acquavita, A., Predonzani, S., Faganeli, J., 2007. Transport and dispersion of particulate Hg associated to a river plume in coastal Northern Adriatic environments. Marine Pollution Bulletin 55, 436–450.

Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M., 2008. Benthic fluxes of mercury species in a lagoon environment (Grado lagoon, Northern Adriatic Sea, Italy). Applied Geochemistry 23, 529–546.

Covelli, S., Acquavita, A., Piani, R., Predonzani, S., De Vittor, C., 2009. Recent contamination of mercury in an estuarine environment (Marano lagoon, Northern Adriatic, Italy). Estuarine, Coastal and Shelf Science 82, 273–284.

Covelli, S., Emili, A., Acquavita, A., Koron, N., Faganeli, J., 2011. Benthic biogeochemical cycling of mercury in two contaminated northern Adriatic coastal lagoons. Continental Shelf Research 31, 1777–1789.

Covelli, S., Langone, L., Acquavita, A., Piani, R., Emili, A., 2012. Historical flux of mercury associated with mining and industrial sources in the Marano and Grado Lagoon (northern Adriatic sea). Estuarine, Coastal and Shelf Science 113, 7–19.

De Vittor, C., Faganeli, J., Emili, A., Covelli, S., Predonzani, S., Acquavita, A., 2012. Benthic fluxes of oxygen, carbon and nutrients in the Marano and Grado Lagoon (Northern Adriatic Sea, Italy). Estuarine, Coastal and Shelf Science 113, 57–70.

Dyrssen, D., Wedborg, M., 1991. The sulphur–mercury(II) system in natural waters. Water, Air, & Soil Pollution 56, 507–519.

Fantozzi, L., Ferrara, R., Frontini, F.P., Dini, F., 2009. Dissolved gaseous mercury production in the dark: evidence for the fundamental role of bacteria in different types of Mediterranean water bodies. The Science of the Total Environment 407, 917–924.

Fitzgerald, W.F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of mercury. Chemical Reviews 107, 641–662.

Fleming, E.J., Mack, E.E., Green, P.G., Nelson, D.C., 2006. Mercury methylation from unexpected sources: molybdate-inhibited freshwater sediments and an iron-reducing bacterium. Applied and Environmental Microbiology 72, 457–464.

Gagnon, C., Pelletier, M., Mucci, A., Fitzgerald, W.F., 1996. Diagenetic behaviour of methylmercury in organic-rich coastal sediments. Limnology and Oceanography 41, 428–434.

Gagnon, C., Pelletier, E., Mucci, A., 1997. Behaviour of anthropogenic mercury in coastal marine sediments. Marine Chemistry 59, 159–176.

Gårdfeldt, K., Sommar, J., Ferrara, R., Ceccarini, C., Lanzillotta, E., Munthe, J., Wängberg, I., Lindqvist, O., Pirrone, N., Sprovieri, F., 2003. Evasion of mercury from coastal and open waters of the Atlantic Ocean and the Mediterranean Sea. Atmospheric Environment 37, 73–84.

Giani, M., Rampazzo, F., Berto, D., Maggi, C., Mao, A., Horvat, M., Emili, A., Covelli, S., 2012. Bioaccumulation of mercury in reared and wild *Ruditapes philippinarum* of a Mediterranean lagoon. Estuarine, Coastal and Shelf Science 113, 116–125.

Gill, G.A., Bloom, N.S., Cappellino, S., Driscoll, C.T., Dobbs, C., McShea, L., Mason, R., Rudd, J.W.M., 1999. Sediment–water fluxes of mercury in Lavaca Bay, Texas. Environmental Science & Technology 33 (5), 663–669.

Gilmour, C.C., Henry, E.A., Mitchell, R., 1992. Sulfate stimulation of mercury methylation in freshwater sediments. Environmental Science & Technology 26, 2281–2287.

Gobeil, C., Cossa, D., 1993. Mercury in sediments and sediment pore water in the Laurentian trough. Canadian Journal of Fisheries and Aquatic Sciences 50, 1794–1800.

Goñi, M.A., Teixeira, M.J., Perkey, D.W., 2003. Sources and distribution of organic matter in a river dominated estuary (Winyah Bay, SC, USA). Estuarine, Coastal and Shelf Science 57, 1023–1048.

Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. Methods of Seawater Analysis, second ed. Verlag Chemie, Weinheim.

Hammerschmidt, C.R., Fitzgerald, W.F., Lamborg, C.H., Balcom, P.H., Visscher, P.T., 2004. Biogeochemistry of methylmercury in sediments of Long Island Sound. Marine Chemistry 90, 31–52.

Han, S., Obraztsova, A., Pretto, P., Choe, K.-Y., Gieskes, J., Deheyn, D.D., Tebo, B.M., 2007. Biogeochemical factors affecting mercury methylation in sediments of the Venice Lagoon, Italy. Environmental Toxicology and Chemistry 26, 655–663.

Hedges, J.I., Keil, R.G., Benner, R., 1997. What happens to terrestrial organic matter in the ocean? Organic Geochemistry 27, 195–212.

Hines, M.E., Faganeli, J., Planinc, R., 1997. Sedimentary anaerobic microbial biogeochemistry in the Gulf of Trieste, northern Adriatic Sea: influence of bottom layer oxygen depletion. Biogeochemistry 39, 65–86.

Hines, M.E., Faganeli, J., Adatto, I., Horvat, M., 2006. Microbial mercury transformations in marine, estuarine and freshwater sediment downstream of the Idrija mercury mine, Slovenia. Applied Geochemistry 11, 1924–1939.

Hines, M., Poitras, E., Covelli, S., Faganeli, J., Emili, A., Žižek, S., Horvat, M., 2012. Mercury methylation and demethylation in Hg-contaminated lagoon sediments (Marano and Grado Lagoons, Italy). Estuarine, Coastal and Shelf Science 113, 85–95.

Horvat, M., Miklavčič, V., Pihlar, B., 1991. Determination of total mercury in coal fly ash by gold amalgamation cold vapour atomic absorption spectrometry. Analytica Chimica Acta 243, 71–79.

Horvat, M., Bloom, N.S., Liang, L., 1993a. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part I: sediments. Analytica Chimica Acta 281, 135–152.

Horvat, M., Bloom, N.S., Liang, L., 1993b. Comparison of distillation with other current isolation methods for the determination of methyl mercury compounds in low level environmental samples. Part II: water. Analytica Chimica Acta 282, 153–168.

Horvat, M., Covelli, S., Faganeli, J., Logar, M., Mandic, V., Rajar, R., Sirca, A., Zagar, D., 1999. Mercury in contaminated coastal environment: a case study: the Gulf of Trieste. The Science of the Total Environment 237/238, 43–56.

Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonarić, T., Pirrone, N., 2003. Speciation of mercury in surface and deep-sea waters in the Mediterranean Sea. Atmospheric Environment 37, S93–S108.

Kerin, E.J., Gilmour, C.C., Roden, E., Suzuki, M.T., Coates, J.D., Mason, R.P., 2006. Mercury methylation by dissimilatory iron-reducing bacteria. Applied and Environmental Microbiology 72, 7919–7921.

Kim, J.P., Fitzgerald, W.F., 1986. Air portioning of mercury in the equatorial Pacific Ocean. Science 23, 1131–1133.

Kim, J.P., Fitzgerald, W.F., 1988. Gaseous mercury profiles in the tropical Pacific Oceans. Geophysical Resource Letters 15, 40–43.

Lambertsson, L., Nilsson, M., 2006. Organic material: the primary control on mercury methylation and ambient methyl mercury concentrations in estuarine sediments. Environmental Science & Technology 40, 1822–1829.

Liang, L., Horvat, M., Bloom, N.S., 1994a. An improved method for speciation of mercury by aqueous phase ethylation, room temperature precollection, GC separation and CVAFS detection. Talanta 41, 371–379.

Liang, L., Bloom, N.S., Horvat, M., 1994b. Simultaneous determination of mercury speciation in biological materials by GC/CVAFS after ethylation and room-temperature precollection. Clinical Chemistry 40, 602–607.

Marvin-DiPasquale, M.C., Lutz, M.A., Brigham, M.E., Krabbenhoft, D.P., Aiken, G.R., Orem, W.H., Hall, B.D., 2009. Mercury cycling in stream ecosystems. 2. Benthic methylmercury production and Bed sediment–pore water partitioning. Environmental Science & Technology 43, 2556–2563.

Mason, R.P., Fitzgerald, W.F., Hurley, J.P., Hanson, A.K., Donaghay, P.L., Sieburth, J.M., 1993. Mercury biogeochemical cycling in a stratified estuary. Limnology and Oceanography 38, 1227–1241.

Merritt, K.A., Amirbahman, A., 2009. Mercury methylation dynamics in estuarine and coastal marine environments—a critical review. Earth-Science Reviews 96, 54–66.

Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. Marine Chemistry 107, 49–63.

Mosetti, F., 1983. Sintesi sull'idrologia del Friuli-Venezia Giulia. Quaderni dell'Ente Tutela Pesca 6, 1–295.

Muresan, B., Cossa, D., Jezequel, D., Prevot, F., Kerbellec, S., 2007. The biogeochemistry of mercury at the sediment–water interface in the Thau lagoon. 1. Partition and speciation. Estuarine, Coastal and Shelf Science 72, 472–484.

Piani, R., Covelli, S., Biester, H., 2005. Mercury contamination in Marano Lagoon (Northern Adriatic sea, Italy): source identification by analyses of Hg phases. Applied Geochemistry 20, 1546–1559.

Point, D., Monperrus, M., Tessier, E., Amouroux, D., Chauvaud, L., Thouzeau, G., Jean, F., Amice, E., Grall, J., Leynaert, A., Clavier, J., Donard, O.F.X., 2007. Biological control of trace metal and organometal benthic fluxes in a eutrophic lagoon (Thau Lagoon, Mediterranean Sea, France). Estuarine, Coastal and Shelf Science 72, 457–471.

Rajar, R., Zagar, D., Sirca, A., Horvat, M., 2000. Three-dimensional modelling of mercury cycling in the Gulf of Trieste. The Science of the Total Environment 260, 109–123.

Ramieri, E., Barbanti, A., Picone, M., Menchini, G., Bressan, E., Dal Forno, E., 2011. Integrated plan for the sustainable management of the Lagoon of Marano and Grado. Littoral. doi:10.1051/litt/201105008.

Ravichandran, M., 2004. Interactions between mercury and dissolved organic matter – a review. Chemosphere 55, 319–331.

Rolfhus, K.R., Fitzgerald, W.F., 2001. The evasion and spatial–temporal distribution of mercury species in Long Island Sound, CT-NY. Geochimica et Cosmochimica Acta 65, 407–418.

Rolfhus, K.R., Fitzgerald, W.F., 2004. Mechanisms and temporal variability of dissolved gaseous mercury production in coastal seawater. Marine Chemistry 90, 125–136.

Rothenberg, S.E., Ambrose, R.F., Jay, J.A., 2008. Mercury cycling in surface water, pore water and sediments of Mugu Lagoon, CA, USA. Environmental Pollution 154, 32–45.

Sfriso, A., Argese, C., Bettiol, C., Facca, C., 2008. Tapes philippinarum seed exposure to metals in polluted areas of the Venice lagoon. Estuarine, Coastal and Shelf Science 79, 581–590.

Shepard, F.P., 1954. Nomenclature based on sand–silt–clay ratios. Journal of Sedimentary Petrology 24, 151–158.

Sirot, V., Guérin, T., Mauras, Y., Garraud, H., Volatier, J.-L., Leblanc, J.-C., 2008. Methylmercury exposure assessment using dietary and biomarker data among frequent seafood consumers in France: CALIPSO study. Environmental Research 107, 30–38.

Sladonja, B., Bettoso, N., Zentilin, A., Tamberlich, F., Acquavita, A., 2011. Manila clam (*Tapes philippinarum*, Adams and Reeve, 1852) in the Lagoon of Marano and Grado (Northern Adriatic Sea, Italy): socio-economic and environmental pathway of a shell farm. In: Sladonja, B. (Ed.), Aquaculture and the Environment – A Shared Destiny, pp. 51–78. www.intechopen.com.

Slowey, A.J., 2010. Rate of formation and dissolution of mercury sulfide nanoparticles: the dual role of natural organic matter. Geochimica et Cosmochimica Acta 74, 4693–4708.