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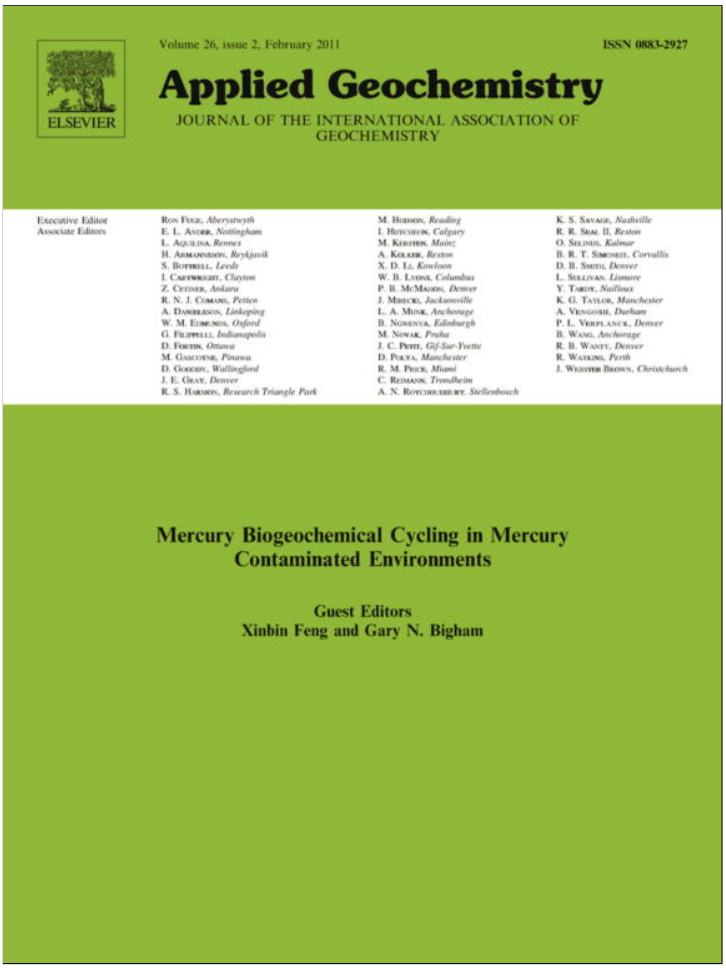

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Does anoxia affect mercury cycling at the sediment–water interface in the Gulf of Trieste (northern Adriatic Sea)? Incubation experiments using benthic flux chambers

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ABSTRACT

Coastal areas in the northernmost part of the Adriatic Sea (Gulf of Trieste and the adjacent Grado Lagoon) are characterized by high levels of Hg, both in sediments and in the water column, mainly originating from the suspended material inflowing through the Isonzo/Soča River system, draining the Idrija (NW Slovenia) mining district, into the Gulf of Trieste. Hypoxic and anoxic conditions at the sediment–water interface (SWI) are frequently observed in the Gulf of Trieste and in the lagoon, due to strong late summer water stratification and high organic matter input. Mercury mobility at the SWI was investigated at three sampling points located in the Gulf of Trieste (AA1, CZ) and in the Grado Lagoon (BAR). Experiments were conducted under laboratory conditions at *in situ* temperature, using a dark flux chamber simulating an oxic–anoxic transition. Temporal variations of dissolved Hg and methylmercury (MeHg) as well as O_2, NH_4^+, $NO_3^- + NO_2^-$, PO_4^{3-}, H_2S, dissolved Fe and Mn, dissolved inorganic C (DIC) and dissolved organic C (DOC) were monitored simultaneously. Benthic Hg fluxes were higher under anoxic conditions than in the oxic phase of the experiment. Methyl Hg release was less noticeable (low or absent) in the oxic phase, probably due to similar methylation and demethylation rates, but high in the anoxic phase of the experiment. The MeHg flux was linked to SO_4 reduction and dissolution of Fe (and Mn) oxyhydroxides, and formation of sulphides. Re-oxygenation was studied at sampling point CZ, where concentrations of MeHg and Hg dropped rapidly probably due to re-adsorption onto Fe (Mn) oxyhydroxides and enhanced demethylation. Sediments, especially during anoxic events, should be, hence, considered as a primary source of MeHg for the water column in the northern Adriatic coastal areas.

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1. Introduction

Marine coastal environments are subject to contamination by several toxic compounds. Among the most concerning pollutants, Hg, a metal with neurotoxic effects on humans (Guzzi and La Porta, 2008), can be transformed in the more toxic and potentially bioaccumulable organometallic form monomethylmercury (MeHg). Evidence suggests that coastal sediments often act both as a repository and a source for Hg of natural and anthropogenic origin (Bloom et al., 1999; Covelli et al., 1999). Moreover, anoxic sediments are a significant source of MeHg for marine food webs (Bloom et al., 1999; Cossa and Gobeil, 2000) since they are recognized to be the main site for microbial Hg methylation, in the presence of SO_4-reducing (Compeau and Bartha, 1985; Gilmour et al., 1992; King et al., 1999; Mason and Lawrence, 1999) and dissimilatory Fe-reducing bacteria (Fleming et al., 2006; Kerin et al., 2006; Schaefer and Morel, 2009).

The Gulf of Trieste, and the adjacent Grado and Marano Lagoon, both located in the northern Adriatic Sea, have been affected by Hg contamination due to the polluted water inputs from the Soča/Isonzo drainage basin. The river is considered to be the largest contributor of Hg into the northern Adriatic Sea since the 16th century, due to its transport of cinnabar rich tailings from the Idrija mining district, located in the northwestern part of Slovenia (Covelli et al., 2001, 2008). The Idrija Hg mine operated for nearly 500 years, until it definitively closed in 1996. Mercury production was second only to Almadén (Spain), the largest Hg mine in the world. It has been estimated that over 5 million metric tons of Hg ore were excavated, of which roughly 73% was recovered (Gosar et al., 1997) while the remainder was dispersed and accumulated in soils, riverbanks and river sediments. Mercury is still being delivered through river flow

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to the Gulf of Trieste (Horvat et al., 1999; Faganeli et al., 2003; Covelli et al., 2006a, 2007), where bottom sediments show Hg concentrations ranging from 0.10 to 23.3 μg g^{-1} against the estimated natural background of 0.13 μg g^{-1} (Covelli et al., 2006b). The Soča/Isonzo River is also responsible for the high Hg concentrations found in sediments of the adjacent Grado and Marano Lagoon, (Covelli et al., 2001, 2008), which range from 2.34 to 10.6 μg g^{-1} and progressively decrease westwards.

Coastal hypoxia events are widespread and increasingly common phenomena, often resulting in seasonal or persistent "dead zones" (Diaz and Rosenberg, 2008). Under low O_2 conditions, Hg methylation is enhanced (Fitzgerald et al., 2007; Merritt and Amirbahman, 2009), with possible negative effects on the marine ecosystem (Fitzgerald et al., 2007).

Hypoxic/anoxic conditions at the sediment–water interface (SWI) have been frequently observed in the Gulf of Trieste as a consequence of high loadings of 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 methylation. While several studies have been conducted on the content and speciation of Hg in marine sediments of the Gulf of Trieste (Biester et al., 2000; Covelli et al., 2001), knowledge of biogeochemical dynamics governing benthic Hg recycling and its transformation in MeHg is limited to only one *in situ* observation (Covelli et al., 1999). The incubation of a sediment under controlled laboratory conditions of temperature, light and O_2 supply is a common way to monitor the behavior of benthic systems under changing redox conditions (Ogrinc and Faganeli, 2006; Belias et al., 2007; Covelli et al., 2008). It is therefore possible to simulate hypoxia/anoxia events occurring at the SWI, to observe the biogeochemical behavior of dissolved compounds and to quantify their release to or scavenging from the water column, due to O_2 depletion.

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. In addition, to better understand the redox processes occurring in the incubated system, water samples were analyzed for nutrients (N and P), Fe and Mn, dissolved inorganic C (DIC) and dissolved organic C (DOC). Nutrients and DIC are products of the degradation and remineralization of organic matter, which is responsible for O_2 depletion and the release of solutes in the water column and can give information on the redox status of the system. Iron and Manganese are very sensitive to changing redox conditions and are involved in important reactions which can be crucial in the fate of Hg species in aquatic systems. DOC is thought to be an important Hg complexing agent (Benoit et al., 2001).

Following the results of a first incubation experiment, it was decided to work on less contaminated sediments from a different experimental site, and to evaluate the effects of re-oxygenation by opening the chamber after an incubation period of two weeks. Results were also compared with data from a previous incubation experiment run for the Grado Lagoon (Covelli et al., 2008) in order to obtain experimental information on the enhancing or limiting factors for Hg and MeHg release in these different sedimentary environments.

2. Study area

The Gulf of Trieste and the Grado and Marano Lagoon (Fig. 1) are both located in the north-eastern Adriatic Sea. The former

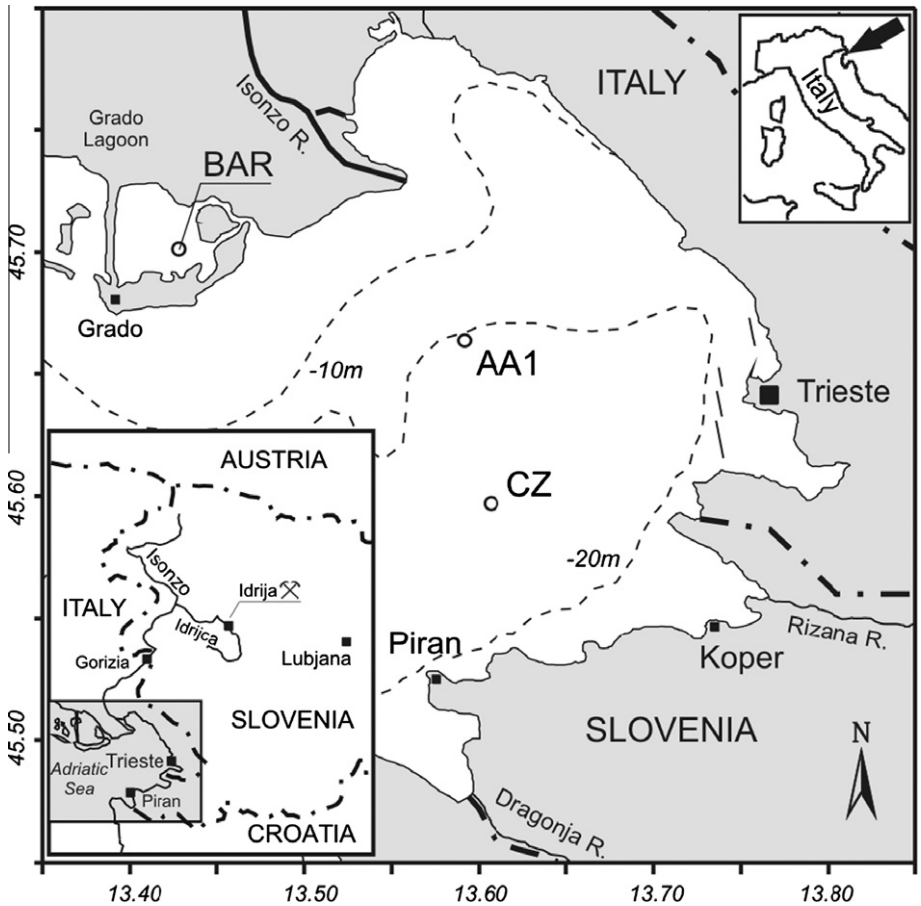

Fig. 1. Location of sampling sites for incubated benthic chamber experiments in the Gulf of Trieste (AA1 and CZ) and in the Grado Lagoon (BAR).

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covers an area of about 600 km^2. The Gulf is a shallow coastal basin, reaching a maximum of about 25 m only in its central part. The water circulation system, which is affected by the action of winds (ENE) and tides (average and spring ranges of 0.5 and 1 m, respectively), is anticlockwise and acts on deep water layers flowing permanently at 2–3 cm s^{-1}. Wind-driven superficial currents differentiate the uppermost water mass, down to a depth of about 5 m, flowing anticlockwise with easterly winds and clockwise with westerly winds (Stravisi, 1983).

The Isonzo River is the main freshwater input. The average annual flow rate at the river mouth estimated for the period 1998–2005 was 91.2 m^3 s^{-1} (1.1–665.9 m^3 s^{-1}; Comici and Bussani, 2007). The riverine discharge shows significant seasonal variations, with two typical flood events governed by snowmelt and rainfall: a relatively long spring maximum (March–May) and a shorter, but more intense, autumn maximum (September–November), when the rate of flow can exceed 2500 m^3 s^{-1} (RAFVG, 1986). The estimated average sedimentation rate obtained by ^{210}Pb determinations is 1.84–2.1 mm a^{-1} in the mid-Gulf (stations AA1 and CZ; Covelli et al., 2001; Ogorelec et al., 1991), and up to 2.5 mm a^{-1} adjacent to the river mouth (Ogorelec et al., 1991). Fluvial inputs also appear to control primary production throughout the coastal marine system, as high contents of nutrients, especially nitrates, which determine phytoplankton blooms, are associated with the highest river discharges (Malej et al., 1995; Salvi et al., 1998).

The Grado and Marano Lagoon extends for about 32 km, between the Tagliamento and Isonzo River deltas, being up to 5 km in width with a total area of 160 km^2. The lagoon basin is subject to semi-diurnal tidal fluxes (65 cm and 105 cm mean and spring tidal range, respectively). The primary source of suspended sediments arrives from the sea, as the contribution of river deltas, and from erosion of the barrier islands. Small rivers flow into the lagoon, draining waters coming from the spring line and those from irrigation canals. Dispersion of sediments into the lagoon is controlled by tidal fluxes through tidal inlets (Brambati, 1970). Very shallow waters (<1 m, on average) characterize the Grado Lagoon (76 km^2) located in the eastern sector of the system (Fig. 1). Most of the lagoon is covered by tidal flats and saltmarshes and some areas are constantly submerged (tidal channels and subtidal zones). Sediment supply in the Grado Lagoon has been historically provided by the Isonzo River inputs dispersing southwestward from its river mouth and entering the lagoon through the tidal inlets.

3. Materials and methods

3.1. Sampling for incubation experiments

Bottom sediment and the overlying water were collected by a SCUBA diver at experimental stations AA1 (November 2006) and CZ (November 2007) using a cylindrical Plexiglas chamber as a sampler (h = 25 cm, i.d. = 24 cm, wall thickness = 0.6 cm). Careful transportation of the chamber to the laboratory minimized disturbance at the SWI. In the laboratory, the overlying water was drained off and carefully replaced with seawater collected from the bottom layer by means of a Niskin bottle at the same sampling location. The chamber was subsequently incubated in the laboratory, at *in situ* temperatures (16 °C for AA1 and 20 °C for CZ), in a dark room for 40 and 25 days, respectively. The average depth of sediments inside the chamber was 10 cm with about 15 cm of overlying water. The top hole of the chamber was sealed with a lid containing two stopcocks for sample collection. Prior to each sampling, to homogenize the system, water inside the chamber was mixed by a magnetic stirrer for 15 min. Water samples were periodically collected by a plastic syringe and the withdrawn volume of water was compensated by bottom seawater collected *in situ*. For the CZ station experiment, the system was re-oxygenated after 16 days by removing the upper lid of the chamber and leaving the water surface in contact with the atmosphere. Fluxes of solutes from the SWI were calculated by linear regression of the variation of solute concentrations with incubation time in both oxic and anoxic conditions: regression line slopes were multiplied by the chamber water volume and divided by the sediment surface area (Bertuzzi et al., 1996).

3.2. Porewater extraction

In November 2006, a sediment core was also collected from site AA1 by pushing a plastic tube into the sediment (core-t_0, h = 30 cm, i.d. = 13 cm). The core was immediately transported to the laboratory, extruded and sliced (0–1, 1–2, 2–3.5 cm) in a N_2 filled chamber after supernatant water collection. Porewaters were extracted by centrifugation (3500 rpm for 40 min, Heraeus centrifuge) at *in situ* temperatures, subsequently recovered in a N_2 atmosphere, filtered on Millipore Millex HA 0.45 μm pore size filters and finally collected in pretreated vials and stored as required by the standard methods for the solutes of interest until analysis. Sediment samples were freeze dried (Lyph-Lock, Labconco), homogenized and sieved through a 420 μm screen to remove coarse shell debris before analysis. The same procedure was repeated on a second AA1 sediment core, subsampled from the incubated sediment at the end of the incubation experiment (core-t_f).

3.3. Analyses

3.3.1. Solid phase

Analyses of total and organic C (C_{tot}, C_{org}), and total N (N_{tot}) in freeze dried and homogenized sediment samples were performed using a Perkin Elmer 2400 CHN Elemental Analyzer (Hedges and Stern, 1984) at a combustion temperature of 975 °C. For C_{org} a progressive acidification (0.1–1.0 M HCl) was performed. The detection limit for C_{org} and C_{tot} was 0.1%. The precision for C_{tot}, C_{org}, and N_{tot} was 3%.

Total Hg (THg) determination in freeze dried sediments was performed after a total decomposition of the sample, as recommended by Loring and Rantala (1992). About 300 mg of dry sediment were treated with a mixture of HF + *aqua regia* (HNO_3:HCl = 1:3 v/v) in a closed microwave system (Milestone MLS 1200). The obtained solutions were analyzed using the CVAAS technique (Perkin Elmer AAnalyst 100-FIAS) after a reduction step ($NaBH_4$ 3% in NaOH 1%). Accuracy was tested using a certified reference material (CRM; PACS-2 Marine sediment, NRCC). Results obtained were in good agreement with the certified value, being the recovery between 95% and 107% (n = 5). The detection limit for the method was 0.13 μg g^{-1}. The precision expressed as relative standard deviation of at least 3 determinations was 5%.

3.3.2. Dissolved phase

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). The reproducibility of the methods was 5%.

Other parameters in the dissolved phase were determined on samples filtered through a Millipore Millex HA 0.45 μm filter. DIC and DOC determinations were performed using a Shimadzu TOC 5000A analyzer. For DIC determination, samples were injected into the IC instrument port and directly acidified with H_3PO_4 (25%). For DOC analysis, water samples were previously acidified (100 μL 6 M HCl) and, after CO_2 elimination, concentration was determined using a high temperature catalytic method (Sugimura and Suzuki,

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1988). Phosphoric acidification for DIC and combustion conducted at 680 °C on a catalyst bed for DOC, generated CO_2 that was carried to a non-dispersive infrared detector (NDIR). Analysis showed a variation coefficient <2%. The reproducibility of the method was between 1.5% and 3%.

Dissolved total Fe and Mn were determined by GFAAS (Perkin Elmer 5100PC) using $Mg(NO_3)_2$ as a matrix modifier. The detection limit for Fe and Mn was 0.01 μmol L^{-1}. Analyses showed a variation coefficient <4%. Nutrients were determined according to Grasshoff et al. (1983) using a continuous flow segmented system (Bran-Luebbe Autoanalyzer AA3). Detection limits for nutrients were, respectively: 0.5 μmol L^{-1} for $NO_3^- + NO_2^-$ as N, 0.4 μmol L^{-1} for NH_4^+ as N, 0.01 μmol L^{-1} for PO_4^{3-} as P.

Total Hg determination in porewater and overlying water samples was performed after the first step of exposure to ultraviolet light and oxidation with BrCl (0.5 mL/100 mL sample). A pre-reduction using $NH_2OH{\cdot}HCl$ (0.25 mL 30%) was followed by reduction with $SnCl_2$ and Au trapping. Analysis was performed by an LCD Milton Roy CVAFS (Horvat et al., 1991). The limit of detection was 0.2 ng L^{-1}. The reproducibility of the method was 4%, whereas the estimated uncertainty was ±3%. The CRM for THg in pore and marine waters was the BCR 579. The determination of MeHg in water and sediment samples started with water vapour distillation conducted at about 160 °C in a heating block with a distillation rate of 8 mL h^{-1}. The detection step was the same for the water and the sediment and it consisted of aqueous phase ethylation (pH 4.6, 100 μL of acetate buffer, 50 μL $NaBEt_4$ 1%), recollection on Tenax traps at room temperature (t = 15 min, Hg-free N_2), thermal desorption (T = 180 °C) and separation of ethylated species on a GC column (Horvat et al., 1993a,b; Liang et al., 1994a,b). 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. The amount of MeHg spiked to the sample was 50 pg. In very rare cases, when the recovery was below average, the sample was re-analyzed before being corrected for lower recovery. The recovery, on average, was about 80%. The results in each batch were corrected for the recovery factor. The reproducibility, expressed in relative standard deviation, varied from 5% to 10%. To control the accuracy of MeHg determination in sediments, the BCR 580 was used as a CRM. Limit of detection for MeHg in the dissolved phase was 50 pg L^{-1}, whereas in the solid phase it was 50 pg g^{-1}.The precision of MeHg determination in CRMs, expressed as relative standard deviation of at least 3 independent determinations, was 3%.

4. Results and discussion

4.1. Solid phase

Sediment grain size in the three stations is very similar (Tab. 1), consisting of clayey silt as defined by Shepard (1954).

Total C (C_{tot}) content in AA1 ranged from 4.68% to 5.44% in core-t_0, and from 5.49% to 5.91% in core-t_f, increasing downcore (Table 1). Organic C (C_{org}) ranged from 1.37%, in the first cm, to 0.98% decreasing downcore in core-t_0, and from 1.28% to 0.95% in core-t_f. Total N (N_{tot}) values decreased slightly with depth, ranging from 0.18% to 0.14% in core-t_0, and from 0.19% to 0.13% in core-t_f. As reported in Hines et al. (2000), CZ showed a similar pattern for C_{org} and N_{tot}, with slightly lower values. For AA1 the C:N atomic ratio was about 9 in core-t_0. Carbon:Nitrogen ratios >12 are associated with land-derived organic matter, whereas values <10 may be defined as marine autochthonous. Organic matter in AA1 is thus predominantly of marine origin but shows a slight riverine influence.

Total Hg content in the first 3.5 cm at AA1 showed increasing downcore concentrations, similar to those reported in Covelli et al. (1999) and in Hines et al. (2000), ranging from 2.80 μg g^{-1} to 4.02 μg g^{-1} in t_0 and from 2.70 μg g^{-1} to 3.47 μg g^{-1} in t_f. For comparison, Hines et al. (2000) report Hg values at CZ ranging from 0.77 to 0.89 μg g^{-1}. Undoubtedly, total Hg profiles in the two stations are related to the historical mining activity at Idrija (Covelli et al., 2001). Such values are considerably higher than the estimated background for the area (0.13 μg g^{-1}, Covelli et al., 2006b). According to Hines et al. (2000), MeHg constituted about 0.04% (1.07 ng g^{-1}) of total Hg at AA1, and 0.05% (0.39 ng g^{-1}) at CZ in surface sediments (Table 1). Methyl Hg concentration generally decreased downcore.

Sedimentary contents of C_{org} and N_{tot} in the Grado Lagoon ranged from 1.15% to 1.95% and from 0.13% to 0.26%, respectively, with a C:N atomic ratio of about 10 to 12. Total Hg content increased with sediment depth, ranging from 10.6 μg g^{-1} to 12.5 μg g^{-1}; MeHg constituted only a small fraction of THg (from 0.003 to 0.206%), decreasing with depth. However, MeHg contents are significantly higher (from 0.60 to 21.9 ng g^{-1}) than those of AA1 and CZ.

4.2. Porewater chemistry

Unfortunately, the porewater and supernatant water dataset is incomplete due to accidental loss of samples during the analyses.

Porewater concentrations were measured both in core-t_0 and core-t_f (Fig. 2). In AA1, DIC and DOC tended to be higher at t_f, where medium values of 3.53 mmol L^{-1} for DIC and 0.62 mmol L^{-1} for DOC were detected, thus confirming the organic matter degradation processes occurring during the oxic–anoxic transition. This is in agreement with DIC and DOC concentrations measured inside the benthic chamber at the end of the incubation experiment (Fig. 3). Values in BAR at t_0 and t_f were always higher, suggesting a more intense degradation, probably related to the differing quality of the organic matter between the two sites.

In AA1, H_2S was not detectable in core-t_0, both in the overlying water and porewaters. At the end of the experiment, 9.14 μmol L^{-1} in the overlying water and a mean concentration of 0.22 μmol L^{-1} in poreweaters were detected. In the sediment H_2S is produced by bacteria-mediated SO_4 reduction, as a consequence of the sediment–water system shifting to anoxic conditions. In comparison, BAR (lagoon environment) always showed a higher H_2S

Table 1
Environmental conditions of solid-phase chemistry in surface sediments (0–3.5 cm) from the sampling stations in the Gulf of Trieste (AA1 and CZ) and in the Grado Lagoon (BAR).

Location	AA1 Gulf of Trieste	CZ Gulf of Trieste	BAR[c] Grado Lagoon
Water depth	22 m	25 m	1.5 m
Salinity	37.6 PSU	37.2 PSU	32.5 PSU
Temperature	16 °C	20 °C	20 °C
Grain-size (<63 μm)	87–98%[a]	74–86%[b]	88–91%
C_{tot}	4.68–5.44%	4.33–4.58%	6.07–7.47%
C_{org}	0.98–1.37%	0.96–1.09%[d]	1.15–1.95%
N_{tot}	0.14–0.18%	0.13–0.15%[d]	0.13–0.26%
C_{org}/N_{tot} (molar)	7.6–8.9	7.5–8.5[d]	9.8–11.6
S_{tot}	0.13–0.18%[d]	0.09–0.19%[d]	
Hg_{tot}	2.80–4.02 μg g^{-1}	0.77–0.89 μg g^{-1}[d]	10.6–12.5 μg g^{-1}
MeHg	0.16–1.07 ng g^{-1}[d]	0.13–0.39 ng g^{-1}[d]	0.60–21.9 ng g^{-1}

[a] Covelli et al. (2001).
[b] Ogorelec et al. (1991).
[c] Covelli et al. (2008).
[d] Hines et al. (2000).

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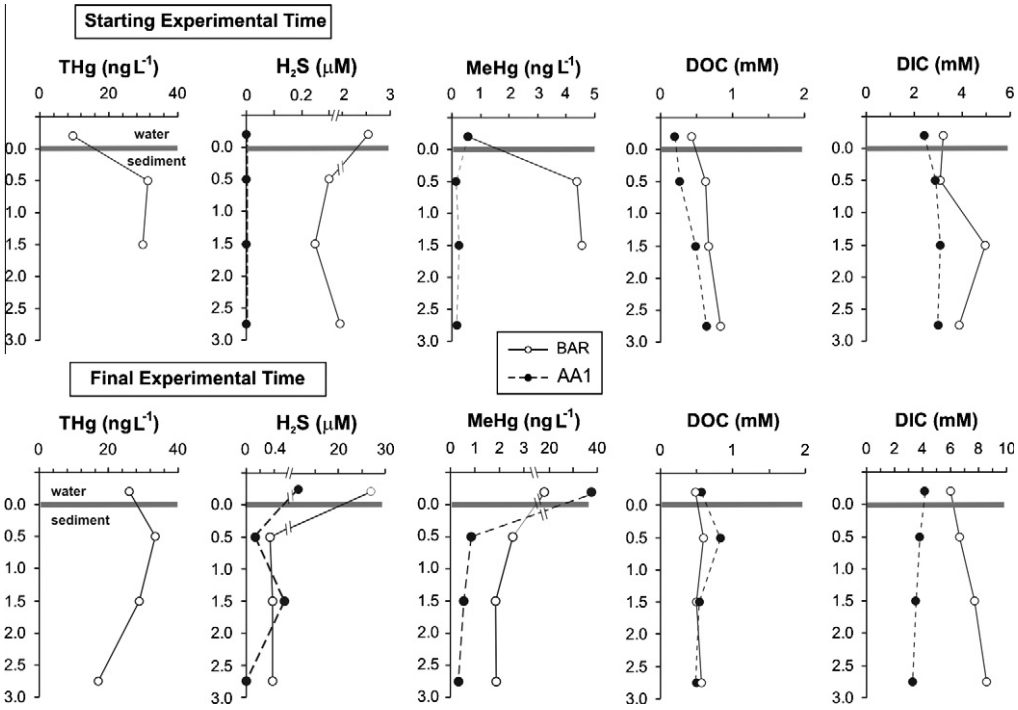

Fig. 2. Porewater concentrations of THg, MeHg, H_2S, DIC and DOC before (starting time) and after (final time) the laboratory incubation experiments for AA1 and BAR sampling stations.

concentration, both in the overlying water and porewaters, as indicative of higher SO_4-reduction activity.

Methyl Hg in AA1 was present in core-t_0, with a concentration of 0.56 ng L^{-1} in the overlying water and a medium value of 0.18 ng L^{-1} in porewaters. In core-t_f, MeHg showed an increased concentration, with a mean value of 0.57 ng L^{-1} in porewaters and a concentration of 37.5 ng L^{-1} in the overlying water. Such an increase in porewater MeHg concentration could be ascribed both to *in situ* Hg methylation and release from the solid phase (e.g. Fe/Mn oxyhydroxides). Methyl Hg in BAR porewaters (Covelli et al., 2008) was always higher than AA1, suggesting that the higher THg content in BAR sediments, as well as more intense SO_4-reduction and organic matter degradation, significantly enhance sedimentary Hg dissolution.

4.3. Behavior of oxygen, DIC, DOC, nutrients, Fe and Mn in benthic flux chambers

The variation of solute concentrations in the benthic chamber during the incubation experiment was measured both in stations AA1 and CZ (Figs. 3 and 4) and compared with the results of the previous experiment conducted in BAR (Covelli et al., 2008). Datasets were distinguished in oxic and anoxic phases on the basis of O_2 concentration. Oxygen concentration less than 32 μmol L^{-1} was considered the limit for the transition from hypoxic to anoxic conditions. Dissolved O_2 in AA1 was quickly consumed by the system, falling from 172 μmol L^{-1} to 24 μmol L^{-1} in 7 days. At t_{10} (27th incubation day), O_2 concentration was not detectable. CZ showed a similar pattern, with O_2 levels falling from 393 μmol L^{-1} at t_0 to non detectable in 7 days. In BAR, O_2 was depleted from an initial concentration of 361 μmol L^{-1} to 43 μmol L^{-1} in 8 days. Oxygen was resupplied to the CZ system by opening the benthic chamber after 16 days of incubation. The effects of re-oxygenation on the benthic chemistry are discussed separately in section 4.5.

DIC concentration inside the AA1 chamber slightly increased, almost linearly, during the experiment, from a starting value of 3.10 mmol L^{-1} at t_0 to 4.13 mmol L^{-1} at t_{13}. Similar patterns were shown by the sediment–water system in CZ, with DIC ranging from 2.50 mmol L^{-1} at t_0 to 3.41 mmol L^{-1} at t_{25}, and in BAR (from 3.16 mmol L^{-1} at t_0 to 6.02 mmol L^{-1} at t_{11}). DOC values in AA1 followed almost the same trend as DIC, increasing linearly from 0.2 mmol L^{-1} to 0.6 mmol L^{-1} at the end of the experiment, while BAR ranged from 0.29 mmol L^{-1} at t_0 to 0.48 mmol L^{-1} at t_{11}.

The NO_3^- + NO_2^- concentration in AA1 fell from 2.21 μmol L^{-1} at t_0 to 0.14 μmol L^{-1} at t_{13}, while NH_4^+ increased constantly from 0.57 μmol L^{-1} at t_0 to 391.05 μmol L^{-1} at t_{13}, thus resulting in NH_4^+ being the dominant N species in the benthic water at the end of the experiment. CZ showed different behavior for the N species. Nitrates and Nitrites were present in the system at t_0 with a concentration of 2.60 μmol L^{-1} which is similar to AA1 but they were not suddenly depleted when O_2 fell below 1 mg L^{-1}. In contrast, NH_4^+ showed a similar behavior to AA1, with its concentration increasing from 7.18 μmol L^{-1} to 228.36 μmol L^{-1} at t_{25} which is similar to the concentration in AA1 at the same incubation time (t_9, 248.05 μmol L^{-1}). Both NO_3^- + NO_2^- and NH_4^+ were higher at t_0 in BAR, compared to the Gulf stations. NO_3^- + NO_2^- smoothly decreased, from the initial 12.79 μmol L^{-1} to 0.34 μmol L^{-1} at t_{11}, while NH_4^+ increased, from 19.06 μmol L^{-1} at t_0 to 396.86 μmol L^{-1} at t_{11}. Given that BAR is a lagoon sediment, it is not surprising to find higher values for nutrients, especially NO_3^-, coming from riverine inputs into the lagoon (ARPA, 2008). CZ was re-oxygenated after t_{18}: the change in the redox conditions did not affect the NH_4^+ concentration in the benthic chamber, which was always positive. The same is true for AA1 and BAR, where the increase in NH_4^+ concentration suggests that N remineralization was occurring in sediment porewaters throughout the redox transition. In shallow marine coastal environments, benthic nutrient regeneration and metabolism are regulated by the quantity and quality of the organic matter supplied to the sediment (Herbert, 1999). The NH_4^+ concentration at the end of the incubation experiments was two orders of magnitude greater than the NO_3^- + NO_2^- concentration, suggesting that ammonification only accounted for a small

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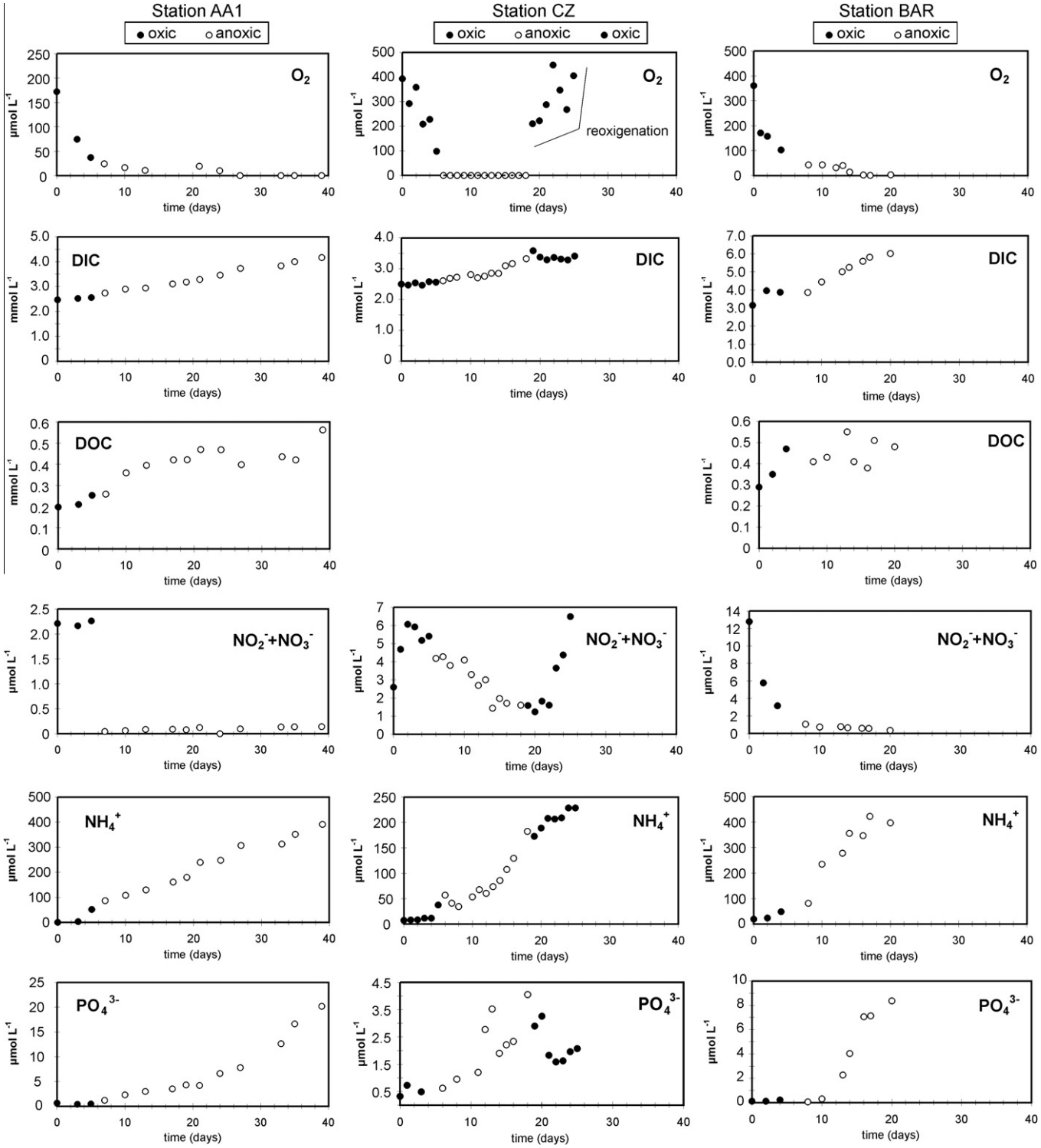

Fig. 3. Evolution of dissolved O_2, DIC, DOC, $NO_2^- + NO_3^-$, NH_4^+ and PO_4^{3-} concentrations in the incubated benthic chamber during the shift from oxic to anoxic conditions. Note that re-oxygenation, after anoxic conditions, was performed for the experiment involving sediment and overlying water sampled at CZ site.

percentage of the NH_4^+ production. Under anoxic conditions, degradation of organic matter should therefore be considered the primary source of NH_4^+ in these sediments. This evidence is also supported by the positive correlation ($r = 0.992$, $n = 12$, $p \leqslant 0.001$) between NH_4^+ and DIC. The sudden consumption of the NO_3^- + NO_2^- pool in AA1 can be explained by the lower concentration of O_2 at t_0 compared to the other stations, as they represent the first alternative electron acceptors used by bacteria in the oxidation of organic matter when oxygen is depleted.

Whereas PO_4^{3-}, in AA1, increased from 0.66 µmol L^{-1} at t_0 to 20.18 µmol L^{-1} at t_{13} (Fig. 3), the same parameter, in CZ, rose from 0.32 µmol L^{-1} at t_0 to 4.05 µmol L^{-1} at t_{18}, the last day of anoxia before re-oxygenation. Under anoxic conditions, P can be released as a consequence of the conversion of the insoluble $FePO_4$ to the

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more soluble $Fe_3(PO_4)_2$. In the Gulf of Trieste, Ogrinc and Faganeli (2006) previously reported an important association between PO_4^{3-} and Fe^{2+}, probably due to the high adsorption capacity of Fe(III) oxyhydroxides for PO_4^{3-} (Lucotte and d'Anglejan, 1988). In this study, PO_4^{3-} parallels Fe^{2+} release in all 3 sites during the early stages of anoxia. Thus, the dissolution of the metal oxides could have contributed to the release of PO_4^{3-} to the water column. Moreover, PO_4^{3-} can also derive from sedimentary organic matter degradation (Nixon, 1981; Fisher et al., 1982; Ogrinc and Faganeli, 2006). This is confirmed by the positive correlation of PO_4^{3-} with NH_4^+ ($r = 0.906$, $n = 12$, $p \leqslant 0.001$) and DIC ($r = 0.938$, $n = 12$, $p \leqslant 0.001$) in AA1.

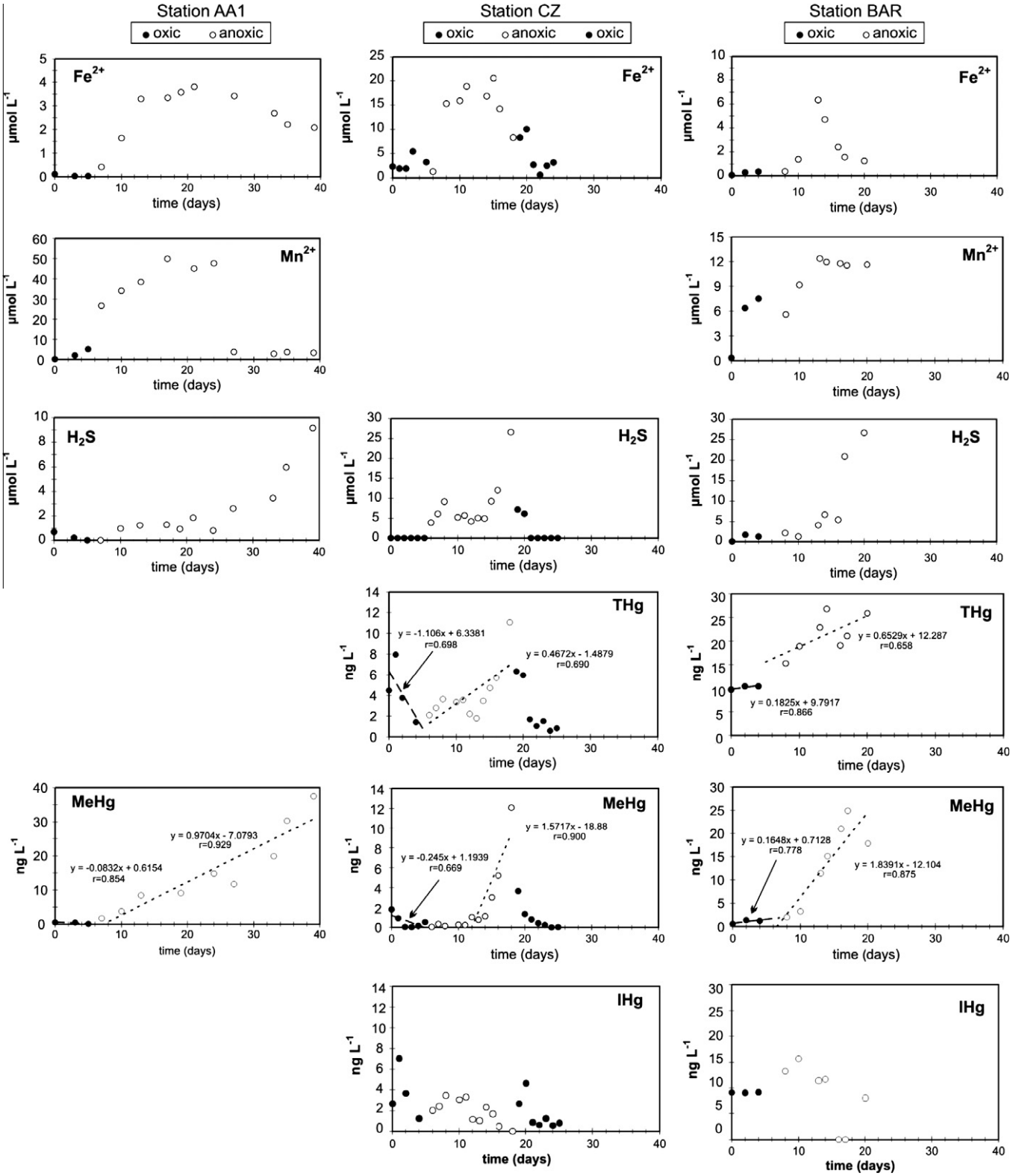

Fig. 4. Evolution of dissolved, Fe^{2+}, Mn^{2+}, H_2S, THg, MeHg and IHg (as THg–MeHg) concentrations in the incubated benthic chamber during the shift from oxic to anoxic conditions. Note that re-oxygenation, after anoxic conditions, was performed for the experiment involving sediment and overlying water sampled at CZ site.

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A rapid increase in Fe^{2+} and Mn^{2+} concentration is showed in AA1, reaching a maximum value of 3.80 μmol L^{-1} for Fe^{2+} and 47.69 μmol L^{-1} for Mn^{2+} (Fig. 4). However, Mn^{2+} was rapidly scavenged from the water column, its concentration falling below 4 μmol L^{-1}, whereas Fe^{2+} decreased less suddenly, to 2.08 μmol L^{-1} at the end of the experiment. CZ and BAR had a similar quick increase for Fe to a maximum of 20.53 μmol L^{-1} in CZ and 6.33 μmol L^{-1} in BAR, but the scavenging from the water column was more rapid and efficient. Manganese(II) in BAR increased promptly during the oxic phase (from 0.33 μmol L^{-1} to 7.52 μmol L^{-1}) and, after a slight decrease in concentration, rose to a plateau (about 11.70 μmol L^{-1}) until the end of the experiment. Overall, the Gulf stations released more Fe^{2+} and Mn^{2+} than the lagoon sediment.

The release of Fe^{2+} and Mn^{2+} from the dissolution of oxyhydroxides and Fe(III) phosphate in the sediment is a possible explanation for their efflux to the water column. The behavior of Fe for station CZ was similar to BAR and AA1 but the higher concentration detected in the benthic chamber suggests that its reduction is much more effective, as a consequence of differences in the sediment geochemistry (more amorphous vs crystalline Fe) and/or in the Fe-reducing bacteria population. High Mn^{2+} fluxes from incubated estuarine sediments, higher than those of Fe^{2+}, have already been reported by Mason et al. (2006). These authors suggested that such behavior could be explained by Mn-oxide dissolution occurring at a higher pε than the Fe-oxides. Manganese reduction occurs earlier than Fe reduction, although reduction and oxidation of the metal are kinetically slower. Iron (II) could have been scavenged either as FeS or FeS_2 (Gagnon et al., 1997), due to the presence of sulfide, and the removal was more effective in BAR and CZ, which had higher H_2S concentrations. In AA1, Mn^{2+} could have precipitated as the poorly soluble $MnCO_3$ ($MnCO_{3(rhodochrosite)} = Mn^{2+} + CO_3^{2-}$; $K_{sp} = 5.01 \times 10^{-10}$, Helgeson et al., 1978). To test this hypothesis, stoichiometric calculations were made. At t_{10}, the ionic product of Mn^{2+} with CO_3^{2-} was equal to the K_{sp} of rhodochrosite and thus the mineral could have formed. The formation of MnS ($MnS_{(alabandite)} + H^+ = HS^- + Mn^{2+}$; $K_{sp} = 3.16 \times 10^{-14}$) was then considered less probable.

In AA1 H_2S increases from 0.68 μmol L^{-1} at t_0 to 9.14 μmol L^{-1} at t_{13}. In CZ, sulfide was produced during the anoxic phase, reaching 26.63 μmol L^{-1} at t_{18} which was the last day before re-oxygenation. BAR sediments also released H_2S, up to 26.69 μmol L^{-1} at t_{11}. Thus, BAR and CZ seem more active in sulfide production than AA1. It has previously been pointed out that AA1 and CZ sediments exhibit a similar SO_4-reduction activity (Hines et al., 2006), while it is higher in BAR (Hines, unpublished data). Within their temperature range of active growth, SO_4-reducing bacteria (SRB) respond to a 10 °C increase in temperature with an increase in their metabolic rate (Q_{10}) by a factor of 2–4, depending on bacteria species present in the sediment and on the availability of SO_4 for reduction (Canfield et al., 2005). Incubation temperatures in AA1 and CZ were, respectively, 16 °C and 20 °C. Thus, a 4 °C difference in temperature between the two experiments could have partially influenced bacterial activity, leading to a higher flux of H_2S from CZ sediments.

4.4. Benthic mercury cycling

4.4.1. Effects of anoxia on mercury species mobility

Dissolved Hg was distinguished in total Hg (THg), MeHg and inorganic Hg (IHg = THg–MeHg) and the results plotted against experimental time (Fig. 4). Unfortunately, THg for AA1 was unavailable. For CZ, during the oxic phase of the experiment, THg decreased in concentration, in parallel with O_2 consumption (Figs. 3 and 4). When O_2 concentration fell to undetectable in 7 days and the system shifted to anoxic conditions, IHg concentration increased to a maximum of about 3.3 ng L^{-1} and then decreased to zero at the end of the anoxic phase. The MeHg:THg ratio shows that, at the end of the anoxic phase of the experiment, the dissolved Hg present in the water column was entirely in the methylated form. Similar behavior has previously been observed for the BAR lagoon sediment (Covelli et al., 2008).

Methyl Hg (Fig. 4) showed a strong increase in concentration both in AA1 (from 0.56 ng L^{-1} at t_0 to 37.50 ng L^{-1} at t_{18}) and CZ (from 1.80 ng L^{-1} at t_0 to 12.06 ng L^{-1} at t_{18}) and it was positively correlated to H_2S in anoxic conditions (Fig. 5), possibly due to Hg methylation by SO_4-reducing bacteria. Despite sediment Hg content being much lower in CZ than the other two stations (Table 1), MeHg mobilization proceeds faster than in AA1. In the same time period (20 days), MeHg in CZ reaches the same concentration as AA1, although an apparent delay in its release and/or production from the sediment was observed. A higher incubation temperature compared to AA1 could have favored bacterial activity, as already suggested for the higher SO_4-reduction. In the early stages of anoxia intense SO_4 reduction could have reduced the availability of neutral Hg–S complexes to methylating bacteria (Benoit et al., 1999) in CZ, limiting MeHg release and explaining the delay.

It has been suggested that organic material and dissolved sulfide are major controls on the availability of Hg(II) to methylating bacteria (Fitzgerald et al., 2007; Hammerschmidt and Fitzgerald, 2008; Merritt and Amirbahman, 2009). In particular, although sulfide can enhance the solubility of inorganic Hg in sediment porewaters, it also reduces the fraction of Hg as HgS^0, the Hg–S complex hypothesized as the most available to bacteria (Benoit

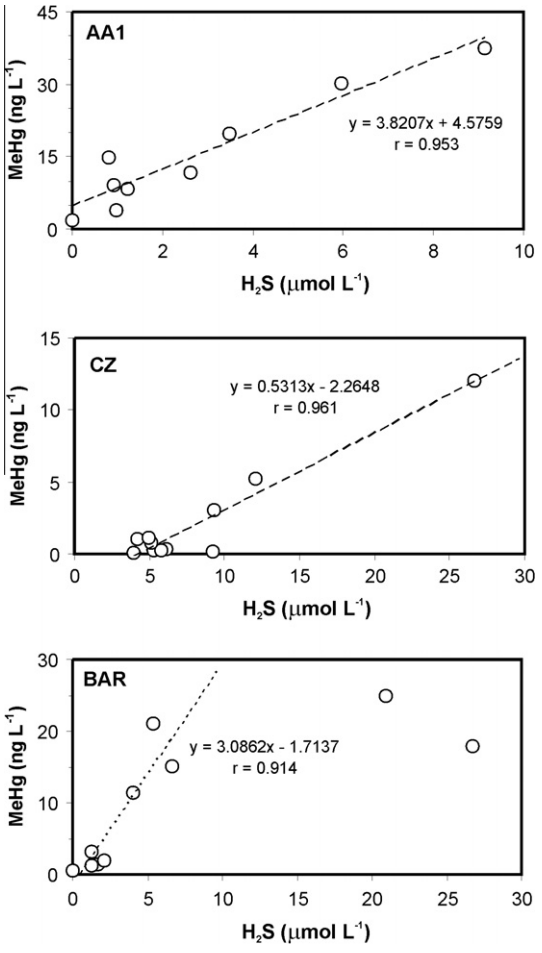

Fig. 5. Relationship between dissolved H_2S and MeHg in the incubated benthic chamber during the anoxic phase in the three experiments. Note differences in scale of the *x* and *y* axes.

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Table 2
Diffusive and *in situ* benthic fluxes of THg, MeHg (expressed in ng m^{-2} day^{-1}) at sites AA1, Gulf of Trieste, and BAR in the Grado Lagoon during autumn.

	Diffusive fluxes				*In situ* benthic fluxes			
	Date	*T* (°C)	THg	MeHg	Date	*T* (°C)	THg	MeHg
Gulf of Trieste (AA1)[a]	October 1996	18	7.29	0.01	October 1996	18	760	3
Grado Lagoon (BAR)[b]	September 2005	20	38.6	16.3	October 2003	21	5896	695

[a] Covelli et al. (1999).
[b] Covelli et al. (2008).

et al., 1999, 2001). Covelli et al. (2008) proposed a similar hypothesis for BAR, where MeHg showed a negative trend in relation to H_2S at the end of the anoxic phase (Fig. 5).

It is likely that in the early stages of anoxia, changes in the redox conditions lead to the dissolution of solid phases, such as Fe oxyhydroxides, in the surface sediment (Mason et al., 2006). In the later stages of anoxia, the redox boundary layer moves towards the top of the sediment, becoming more and more anoxic and active in the efflux of solutes to the water column. Consequently, Hg and MeHg, that were previously scavenged in oxic conditions and sequestered by these phases, are released into the water column. As reported by Fitzgerald et al. (2007), under hypoxic/anoxic conditions, the zone for optimized Hg methylation may also migrate upwards, into the water column. Evidence of MeHg formation in the anoxic water column by bacteria has already been given by other authors (Mason et al., 1993; Monperrus et al., 2007), although the microbial community responsible for methylation was not identified. Thus, the transition from oxic to anoxic conditions and the persistence of a reductive environment in the sediment–water system cause both the sediment (surface and deep) and water column to act as an important source of Hg species for the marine environment.

4.4.2. Mercury and methylmercury fluxes

Significant fluxes of THg and MeHg from sediments of AA1 and BAR (Covelli et al., 1999, 2008) were observed previously during *in situ* benthic chamber experiments (Table 2), which are considered indicative of natural conditions. During the autumn, AA1 and BAR showed positive fluxes of THg and MeHg and sediments at both sites were considered potential release sources of MeHg into the water column (Covelli et al., 1999, 2008). Diffusive fluxes (Table 2) were up to two orders of magnitude lower than *in situ* benthic fluxes, a discrepancy already reported by several other authors (Choe et al., 2004; Point et al., 2007; Hammerschmidt and Fitzgerald, 2008).

Methyl Hg production (difference between Hg methylation and MeHg demethylation) in AA1 and CZ was determined by Hines et al. (2006) using radio-techniques. Using porewater data, the results were in good agreement with *in situ* benthic fluxes reported by Covelli et al. (1999), although the two experimental approaches are quite different.

In all sediment incubation experiments described in the present paper, anoxic conditions seem to favor Hg and MeHg release to the water column (Table 3). For AA1 and CZ, MeHg fluxes are higher than both *in situ* benthic fluxes (Table 2) and MeHg production determined by Hines et al. (2006). This evidence suggests that forcing the sediment–water system to prolonged anoxic conditions results in enhanced MeHg release in these coastal environments.

It is also interesting to note that despite a lower Hg content in the sediment, CZ showed higher MeHg fluxes than AA1. On the other hand, fluxes in BAR are always higher than the Gulf stations, both in incubated and *in situ* benthic experiments. Thus, lagoon sediments seem more active in the remobilization of Hg and MeHg than the Gulf sediments. However, fluxes in the lagoon are not as high as expected given the larger amount of Hg in the sediments, thus showing that it is not strictly dependent on the total concentration of the element.

Table 3
Benthic fluxes of THg, MeHg (expressed in ng m^{-2} day^{-1}) calculated for sites AA1 and CZ (Gulf of Trieste) and BAR (Grado Lagoon) from the incubation experiments performed during autumn. Negative values indicate influxes.

	Date	*T* (°C)	THg fluxes		MeHg fluxes	
			Oxic	Anoxic	Oxic	Anoxic
Gulf of Trieste (AA1)	November 2006	16	n.a.	n.a.	−12	147
Gulf of Trieste (CZ)	November 2007	20	−167	71	−37	238
Grado Lagoon (BAR)[a]	September 2005	20	140	60	34	498

[a] Covelli et al. (2008).

4.5. Benthic chamber re-oxygenation

After two weeks of incubation, the sediment–water system from the CZ station was re-oxygenated by opening the benthic chamber (Fig. 3). Dissolved O_2 increased rapidly, rising from un-detected to 105 μmol L^{-1} at t_{19} and 203 μmol L^{-1} at the end of the experiment (t_{25}), which was similar to the O_2 concentration at the beginning of the incubation period. Following the chamber re-oxygenation, the concentration of NO_3^-+NO_2^- in the water column increased from 1.58 μmol L^{-1} to 6.49 μmol L^{-1}. Ammonium continued to be released from the sediment, reaching 228.36 μmol L^{-1} at the end of the experiment. DIC, which increased during the anoxic phase, stabilized around a concentration of 3.30 mmol L^{-1} which is higher than at the beginning of the experiment (2.50 mmol L^{-1}). Phosphate was scavenged from the water column, decreasing from 4.05 μmol L^{-1} at t_{18} to below 2.00 μmol L^{-1} at t_{21}, possibly precipitated with Fe(III) oxyhydroxides (Ogrinc and Faganeli, 2006). Both H_2S and MeHg showed a rapid decrease in concentration. Sulfides fell from 26.63 μmol L^{-1} at t_{18}, the last day of anoxia, to 7.22 μmol L^{-1} on t_{19}, decreasing to zero. At the same time, MeHg concentration decreased from 12.06 ng L^{-1} on t_{18} to near-zero values. Total Hg also decreased in concentration.

Iron and Manganese oxyhydroxides are effective scavengers of soluble Hg in oxic surface sediments (Gagnon et al., 1997; Muresan et al., 2007) so the formation of authigenic Fe-oxides and the coprecipitation of the Hg species with them is a possible explanation for their decrease in concentration in the re-oxygenated benthic water (Fig. 4). Enhanced demethylation in oxic conditions is a possible explanation for the decreasing percentage of MeHg to total Hg after re-oxygenation, suggesting a transformation of methylated Hg species occurring in the water column, although it can not be excluded that a higher efficiency in MeHg scavenging by Fe/Mn oxyhydroxides, compared to inorganic Hg scavenging, might be responsible for the altered MeHg:THg ratio.

5. Conclusions

The incubation experiments showed that hypoxic and anoxic conditions play a significant role in the remobilization of Hg species in the Gulf of Trieste, in particular methylated forms, with

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significant fluxes from the sediment to the water column. The release of Hg species is probably the result of several processes, such as diffusion from porewaters, dissolution of some fraction of the surface sediment, and Hg methylation.

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 SO_4 reduction in anoxic sediments. Methyl Hg fluxes in the Lagoon are higher than in the Gulf of Trieste, although not as high as expected given the larger amount of Hg in the sediments. In contrast, in the Gulf of Trieste, MeHg fluxes are higher in CZ, despite a lower Hg content than AA1. Thus, MeHg release under anoxic conditions cannot be predicted based only on THg content of the sediment and other factors should be considered to explain Hg and MeHg dynamics at the SWI in these coastal environments.

The re-oxygenation phase in CZ suggests that reversion to oxic conditions removes Hg species from the water column, most probably through precipitation and coprecipitation with Fe and Mn oxyhydroxides. It is also interesting to note that, following re-oxygenation, the percentage of MeHg to total Hg in the water column decreases from 100% to nearly zero. It is conceivable that some demethylation process is occurring in the water column and that Fe/Mn oxyhydroxides scavenging of MeHg is more efficient than on Hg.

The results from this work suggest that a better understanding of the biogeochemical processes governing Hg cycling in these coastal environments could be achieved by focusing on the speciation of Hg in sediments. On the other hand, it should be emphasized that Hg behavior appears to be site specific, thus encouraging further research on the effects of anoxic conditions in different sites.

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