

# A comprehensive assessment of the mercury budget in the Marano–Grado Lagoon (Adriatic Sea) using a combined observational modeling approach



Donata Melaku Canu <sup>a,\*</sup>, Ginevra Rosati <sup>a</sup>, Cosimo Solidoro <sup>a,b</sup>, Lars-Eric Heimbürger <sup>c,e</sup>, Alessandro Acquavita <sup>d</sup>

<sup>a</sup> OGS—National Institute of Oceanography and Experimental Geophysics, Borgo Grotta Gigane 42 c. Sgonico, Trieste, Italy

<sup>b</sup> ICTP, The Abdus Salam International Centre for Theoretical Physics — Strada Costiera, 11 I-34151 Trieste, Italy

<sup>c</sup> Geochemistry and Hydrogeology Group, Department of Geosciences, University of Bremen Klagenfurter Straße, 28359 Bremen, Germany

<sup>d</sup> O.A.A. — Osservatorio Alto Adriatico Via Lamarmora, 13–34139 Trieste, TS, Italy

<sup>e</sup> Mediterranean Institute of Oceanography Campus de Luminy, 13288 Marseille, France

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## ABSTRACT

In this study, a biogeochemical model of the mercury cycle is applied to the Marano–Grado Lagoon (North Adriatic Sea, Italy) to 1) integrate the ensemble of disconnected and snap shot measurements collected over the last decade into a common and coherent framework, 2) assess the concentration of mercury species ( $\text{Hg}^{\text{II}}$ ,  $\text{MeHg}$ ,  $\text{Hg}^0$ ) in water, sediment and particulates, and 3) quantify the mercury fluxes and budgets within the lagoon and among the lagoon, the atmosphere and the Adriatic Sea. As a result of long-term industrial and natural contamination, the Marano–Grado Lagoon is a hot spot of mercury contamination in the Mediterranean Region. Several monitoring activities have been undertaken to evaluate the environmental impacts and to better understand mercury cycling in this region. We used the results from these studies to build a mercury biogeochemical model and assess its ability to accurately predict mercury concentrations and fluxes. The results indicate that 1) the lagoon is a contaminated site, with water and sediment concentrations of Hg and MeHg higher than those of comparable environments; 2) there is substantial production of MeHg favored high productivity, occurrence of seasonal anoxia, and shallow conditions; and 3) the lagoon is a source of mercury contamination for the Mediterranean Sea, contributing to about 5% of the total  $\text{Hg}_T$  load. Research also indicates that the most critical shortcoming of the currently available data sets is the lack of complete synoptic measurements, even for short time periods. Future research programs must also include information on the photo-transformation rates, such as of photo-reduction, photo-oxidation and photo-demethylation.

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## 1. 1. Introduction

Mercury (Hg) is a persistent pollutant of global concern that is mainly emitted as the volatile elemental form  $\text{Hg}^0$  from anthropogenic and natural sources. Upon oxidation to  $\text{Hg}^{2+}$ , Hg deposits on land and oceans, where it can undergo multiple biotic and abiotic transformations, such as photochemical and microbial reduction as well as microbial methylation to organic methylmercury (MeHg) (Sonke et al., 2013). Biological MeHg production (methylation) and degradation (demethylation) in coastal environments occur predominantly in sediment (Monperrus et al., 2007a; Merritt and Amirbahman, 2009 and references therein). However, there is increasing evidence of MeHg biotic production in oxic surface water, especially during or after periods of high productivity when heterotrophic activity is elevated (Bouchet et al., 2013;

Heimbürger et al., 2015; Heimbürger et al., 2010; Lehnher et al., 2011; Monperrus et al., 2007a; Monperrus et al., 2007b; Sharif et al., 2014).

MeHg is assimilated by living organisms and tends to bioaccumulate and biomagnify along freshwater and marine trophic webs (Watrass et al., 1998; Cossa et al., 2012). Human MeHg exposure can subsequently occur through fish intake (Black et al., 2012; Fitzgerald et al., 2007; Mason et al., 2012; Sunderland et al., 2009). The health risks for human and wildlife posed by chronic exposure to MeHg and its related socio-economic consequences have led to an increase in attention to this issue. The health risks for human and wildlife posed by chronic exposure to MeHg and its related socio-economic consequences have led to an increase in attention to this issue, such as those agreed upon by the United Nation Environment Programme (UNEP) during the Minamata Convention. These global efforts to reduce anthropogenic Hg emissions highlight the importance of this issue and there has been a concerted effort among researchers to quantify the concentration and flux of Hg species and understand Hg transformations. We

\* Corresponding author.

now have abundant field observations that can be modeled in an effort to develop predicative models to assess long-term ecological impacts and to better focus future research efforts.

Hg is a pollutant of great concern in the North Adriatic Sea, particularly in the Marano–Grado Lagoon, where high productivity, occurrence of seasonal anoxia, and shallow conditions could promote the transformation of Hg into bio-available compounds, as previously observed in other shallow lagoon systems (Bloom et al., 2004; Monperrus et al., 2007a, 2007b). To date, the dynamics of Hg species in the benthic compartment of this lagoon have been investigated in some detail (Acquavita et al., 2012a; Bramabati, 1996; Covelli et al., 2012; Covelli et al., 2008a, 2008b; Emili et al., 2012; Giani et al., 2012; Hines et al., 2012; Piani et al., 2005), although a limited number of sampling stations have been considered in most cases and the emerging data are fragmented. Less is known regarding the fate of Hg species in water columns. In this media, several transformations can occur (i.e., photo-reduction, photo-oxidation, photo-demethylation and possibly biotic methylation and demethylation), which can increase Hg evasion, deposition or bioaccumulation rates. The water column is also where bioconcentration by phytoplankton takes place (i.e., the first step of Hg biomagnification in the pelagic trophic web. Therefore, collating and integrating the available information into a common framework would be timely and useful for enhancing our current understanding of Hg pollution, identifying possible gaps, and informing effective management policies.

Characterizing Hg speciation and fluxes among environmental compartments is difficult, expensive and time consuming. Consequently, even in hot spot environments, data sets are often incomplete, and robust measurement assessments are often unavailable. Moreover, quantifying the transfer of Hg from environmental matrices to biota is a challenging task. Simple correlative approaches do not give a correct assessment of bioaccumulation because environmental parameters influence transfer kinetics. Modeling approaches may help overcome some of these limitations and are highly encouraged (Sonke et al., 2013; Black et al., 2012), although the lack of comprehensive data sets often hinder the development and application of models (Black et al., 2012). Currently a few attempts have been made to model the budget and biogeochemical cycling of total Hg in marine environments at global, regional and subregional scales (Amos et al., 2014; Soerensen et al., 2014; Sunderland et al., 2009), including the Mediterranean Sea (Rajar et al., 2007; Žagar et al., 2007). However, additional efforts are needed to model MeHg budgets in coastal areas (Bloom et al., 2004), where more accurate quantification of pollutant sources, transformation, and transport would be required.

Hg cycling in the Marano–Grado Lagoon has been previously modeled with the 0-D model SERAFM (Melaku Canu et al., 2012) to compile an initial overview of the processes that govern Hg fluxes into and out of the lagoon and to assess the relative importance of different contamination sources. However, this model lacked the ability to resolve spatial and temporal trends/characteristics. Incorporating finer spatial and temporal resolutions into the model would generate a better representation of local characteristics such as biogeochemical and transport processes and would improve the Hg model to provide a better assessment of the fluxes of Hg species among the compartments. However, this would also require more information on the spatial distribution of chemical and biogeochemical parameters and processes, as well as detailed information on the hydrology, and solid transport within the system. Therefore, a sensible trade-off is needed. Here, we decided to model Hg dynamics by subdividing the lagoon in 21 boxes, and the transport between boxes was modeled using a high-resolution hydrodynamic model.

In this study, we collated available information on the Hg cycle in the Marano–Grado Lagoon, estimated missing information through an extensive literature review, and implemented the dynamic Hg module of WASP7 (Water Analysis Simulation Program, US EPA, 1988) to

investigate Hg dynamics and establish a mass balance. We also aimed to determine whether and to what extent the lagoon could represent a site of net MeHg production and a secondary source of bioavailable Hg contamination to the Adriatic.

### 1.1. Study area

The Marano–Grado Lagoon (Northern Adriatic Sea, Italy) is a large wetland environment in the Mediterranean region (Fig. 1). It covers an area of 160 km<sup>2</sup> and provides important ecosystem services, which sustains economic development, tourism, and fishery activities. The watershed supports approximately 32,000 inhabitants (Pirastu et al., 2014). The lagoon is an optimal nursery and recruitment zone for some fish species and provides shelter to many bird colonies. It has been recognized as a Special Area of Conservation (SAC – IT3320037) by the EU Habitat Directive 92/43/EEC.

The lagoon dynamically exchanges water with the Northern Adriatic Sea through six inlets, namely Lignano, S. Andrea, Buso, Morgo, Grado and Primero (Fig. 1). An increasing salinity gradient occurs from the inland regions of the lagoon toward the inlets. Due to its shallowness, the lagoon also experiences strong seasonal fluctuations in water temperature spanning from approximately 0 to 30 °C.

The western and the eastern sectors, also called the Marano and Grado Lagoons, exhibit some different physico-chemical features: the Marano Lagoon receives a greater input of freshwater from its tributaries (Stella, Turgnano, Zellina, Cormor, Corno–Aussa rivers) and is characterized by lower salinity and higher nutrient concentrations compared with the Grado Lagoon, which receives small freshwater inputs from the Natissa River (Fig. 1). The Grado Lagoon is shallower, and presents weaker hydrodynamics and more complex morphologies such as saltmarshes and a tidal flat.

The Marano–Grado Lagoon acts as a sink for various contaminants released from different anthropogenic activities, including large amounts of Hg compounds that have led to high total Hg (Hg<sub>T</sub>) concentrations in the lagoon sediment (2.49–69.8 nmol/g; Acquavita et al., 2012a, 2012b; Regional Protection Agency–Friuli Venezia Giulia–ARPAFVG), pore water (Covelli et al., 2008a, 2008b; Emili et al., 2012) and local biota (Bramabati, 1996; Giani et al., 2012). Sediment values are 10 to 280 times higher than those of the open Mediterranean Sea sediments (Heimbürger et al., 2012).

The historic source of Hg was the Idrija cinnabar mine in western Slovenia, which operated from the 16th century until 1994. Dizdarevič (2001) estimated that approximately 37,000 tons of Hg (equivalent to  $1.84 \times 10^5$  Kmol of Hg) were discharged during the lifetime of the mine. Much of the released Hg persists in the Soča/Isonzo River banks and is slowly released into the Gulf of Trieste (the northern part of Adriatic Sea), especially during flooding events. Once Hg reaches the Gulf of Trieste, it is transported through general water circulation and in the sediment. When the river plume is diverted to the SW under the influence of E–NE winds, the tidal flux carries particulate Hg (Hg<sub>p</sub>), which is mostly inorganic, into the Grado Lagoon (Covelli et al., 2007). The second most relevant Hg source is a chlor-alkali plant (see Fig. 1) that dumped approximately 190 tons of Hg (equivalent to  $9.5 \times 10^2$  Kmol) directly into the lagoon through the Aussa–Corno River (Acquavita et al., 2012a, 2012b) during its 45 years of operation. As a result of historical and more recent Hg emissions, it is estimated that 251 tons of Hg (equivalent to  $1.25 \times 10^3$  Kmol) are buried in the sediments of the lagoon (Covelli et al., 2012). Therefore, the lagoon sediment, together with the sediment stored in the Aussa–Corno River and in the Gulf of Trieste, has the potential to act as a secondary source of Hg.

## 2. Materials and methods

To investigate Hg cycle dynamics and estimate Hg species fluxes in the Marano–Grado Lagoon ecosystem, we implemented the water quality model WASP7, which was released by the US EPA and is publicly



Fig. 1. The Marano–Grado Lagoon with its six sub-basins outlined in yellow. Light blue arrows indicate transport by water masses. The two main sources of contaminations are shown as well.

available at the web site <http://www2.epa.gov/exposure-assessment-models/surface-water-models> (last visit 13/01/2015).

### 2.1. The WASP model

The WASP7 model is a dynamic process-based water quality model made of different sub-models, including one for Hg (MERC7). This model can reproduce the temporal and spatial evolution of three Hg species ( $\text{Hg}^{\text{II}}$ , MeHg,  $\text{Hg}^0$ ) concentrations in water, pore water and sediments, accounting for their partition into dissolved phases ( $\text{Hg}_D$  and  $\text{MeHg}_D$ , which include both the ionic form and the DOC-complexed fraction) and particulate phases ( $\text{Hg}_P$  and  $\text{MeHg}_P$ , which include silt, sand and organic matter sorbed fractions), as illustrated in Fig. 2.

The model allows users to discretize a water body in one, two or three dimensions, by means of interconnected zero dimensional boxes, which represent water or sediment compartments. The overall

equation (Eq. (1.1)) for the mass conservation of the state variables in each water box includes terms for advection ( $U$  in m/s) and diffusion ( $E$  in  $\text{m}^2/\text{day}$ ) in the three dimensions ( $x, y, z$ ). It also accounts for direct or diffusive loads ( $S_L$  in  $\text{g}/\text{m}^3$  day), exchanges with the boundaries or the sediment ( $S_B$  in  $\text{g}/\text{m}^3$  day) as well as the biochemical or photochemical transformation of Hg species ( $S_{rx}$  in  $\text{g}/\text{m}^3$  day):

$$\frac{dC}{dt} = \frac{d(U_x C)}{dx} - \frac{d(U_y C)}{dy} - \frac{d(U_z C)}{dz} + \frac{d}{dx} \left( E_x \frac{dC}{dx} \right) + \frac{d}{dy} \left( E_y \frac{dC}{dy} \right) + \frac{d}{dz} \left( E_z \frac{dC}{dz} \right) + S_L + S_B + S_{rx}. \quad (1.1)$$

Hence, the exchange of water, Hg species and suspended particulate matter between water boxes, as well as those between boxes and boundaries, depend on advection and dispersion processes. While it is being subjected to transport, Hg species can undergo several biotic or

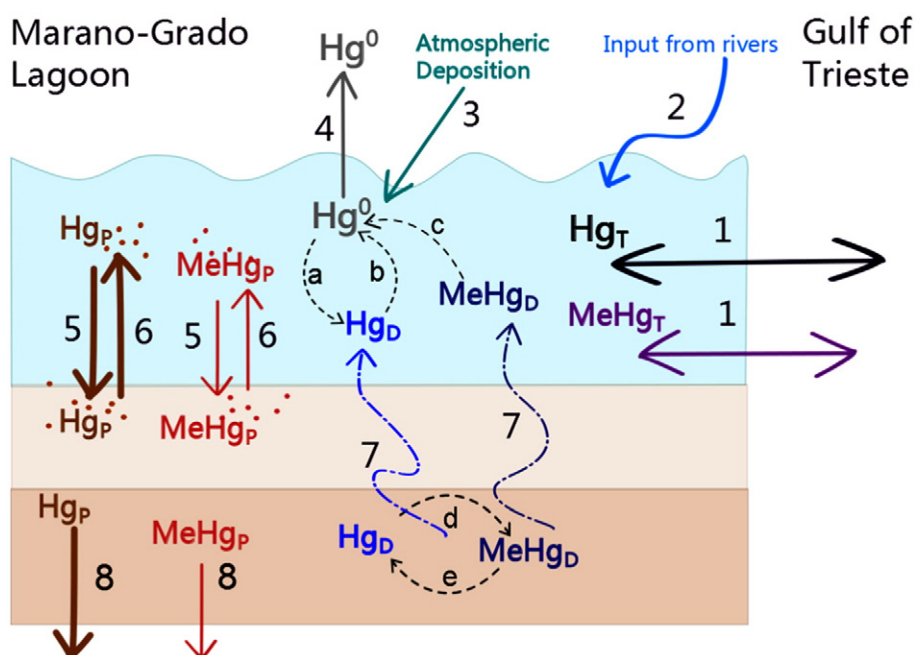


Fig. 2. Main transport (1—exchange with the sea, 2—input from rivers, 3—atmospheric deposition, 4—volatilization, 5—deposition, 6—resuspension, 7—pore water diffusion, 8—burial) and transformation (a—photo-oxidation, b—photo-reduction, c—photo-demethylation, d—methylation, e—demethylation) processes included in the WASP model.  $\text{Hg}_T$  is total Hg ( $\text{Hg}^{\text{II}} + \text{Hg}^0 + \text{MeHg}$  in dissolved and particulate phase),  $\text{MeHg}_T$  is total MeHg (dissolved and particulate phase of MeHg),  $\text{Hg}_P$  and  $\text{MeHg}_P$  are particulate-bounded  $\text{Hg}^{\text{II}}$  and MeHg, whilst  $\text{Hg}_D$  and  $\text{MeHg}_D$  are the dissolved forms of  $\text{Hg}^{\text{II}}$  and MeHg.



light-mediated transformations (i.e., microbial methylation and demethylation, dark oxidation, photo-reduction, photo-oxidation and photo-demethylation).

Dissolved elemental Hg ( $Hg_w^0$ ) is exchanged between the surface water boxes and the overlying atmosphere ( $Hg_{atm}^0$ ) with a rate ( $Ae$ ) that depends on the water and air concentrations of elemental Hg ( $Hg_w^0$  and  $Hg_{atm}^0$  in mg/L), Henry's law constant  $H$ , the universal gas constant  $R$ , the temperature value in degrees Kelvin, and the volatilization rate constant ( $K_{vol}$  in 1/d).

$$Ae = k_{vol} \cdot \left( Hg_w^0 - \frac{Hg_{atm}^0}{H/RT} \right). \quad (1.2)$$

Movements of Hg species from the sediment layer to the water, and vice versa, are controlled by deposition and resuspension rates of organic and inorganic solids as well as by pore water diffusion. In surface sediment boxes, the mass variation ( $dm_k/dt$ ) of a solid  $k$  in a box  $j$  (Eq. (1.3)) is computed as the sum of fluxes owing to deposition rates ( $v_d$ , in m/day) of suspended solids ( $M_k^w$  in  $g/m^3$ ) from the water as well as to solid resuspension ( $-v_{rs}$ , in m/day) and burial rates ( $-v_b$ , in m/day) of the sediments ( $M_k^j$ , in  $g/m^3$ ). In sub-surface layers ( $jj$  boxes, Eq. (1.4)), the balance depends on the burial rate ( $V_b$ ):

$$d \frac{m_k^j}{dt} = v_d \cdot M_k^w - (v_{rs} + V_b) \cdot M_k^j \quad (1.3)$$

$$d \frac{m_k^{jj}}{dt} = v_b \cdot M_k^j - v_b \cdot M_k^{jj}. \quad (1.4)$$

In each water box  $w$ , the concentration of the adsorbed fraction of a Hg species  $i$  on the solid  $k$ ,  $C_{i,k}^w$ , varies according to the Hg species concentration, solid dynamics and the fraction  $f_{i,k}$  of the chemical species adsorbed, which depends on the partition coefficients of the species between water and solids. Further details on the equations used in the model are provided by Wool et al. (2001).

## 2.2. Available data and model implementation

We implemented the WASP7 model using site-specific data, which were complemented by literature values obtained from similar environments, as summarized in Supplemental Materials. Although many research studies focusing on the Hg cycle have been carried out in the lagoon, a comprehensive investigation has never been performed. We therefore augmented our seasonal database with additional information obtained from projects carried out by the Regional Environmental Protection Agency (ARPA FVG) at the University of Trieste in the Friuli Venezia Giulia Region, and the National Institute of Oceanography and Experimental Geophysics (OGS). We gathered data on meteorological conditions, suspended particulate matter and Hg species concentrations at the lagoon boundaries (i.e., the water/air interface, the river mouths and the lagoon inlets), as well as data regarding Hg distribution, transport processes and transformation rates within the Marano–Grado Lagoon (Supplemental Materials, Table S1) and similar environments (Supplemental Materials, Table S2).

Considering the spatial resolution of available Hg data and the major features of the lagoon environment, the model was implemented starting from the hydrological classification defined by Dorigo (1965). Therefore we represented the lagoon (Fig. 1) with 6 water boxes, each representing a lagoon sub-basin, and 12 sediment boxes, i.e. a surface sediment layer (0–2 cm depth) and a subsurface sediment layer (3–10 cm depth) for each sub-basin. Additionally, there were 3 more water boxes representing the 3 major tributaries. Cross sectional areas between boxes were estimated using the hydrodynamic model. The cross sectional areas between the marine boundaries and the lagoon (i.e., the inlet sections) are given in Fontolan et al. (2007). Gross bulk water exchanges ( $m^3/s$ ) between the 6 water boxes and the marine

boundaries were computed using the 2D hydrodynamical model described in Ferrarin et al. (2010) and were then included in the WASP7 model. Following indications from the WASP7 model (US EPA 1988, US EPA, 2009 and <http://epa.gov/athens/wwwqtsc/courses/wasp7/index.html> last access 04/12/2014) and calibration results, we set the dispersion between water boxes at  $10 m^2/s$ .

The model requires the initial conditions for each of the 21 boxes to be defined. The Hg species concentrations in sediment were initialized according to Acquavita et al., 2012a, 2012b. We discriminated between cinnabar mercury ( $HgS$ ) and the more recent Hg that originated from the chlor-alkali plant by setting different partition coefficient ( $K_D$ ) values (Supplemental Materials, Table S3). In agreement with this choice, the cinnabar form was less susceptible to transformations. Initial concentrations of silt-clay, sand and POM in sediment boxes ( $g/m^3$ ) were computed from the percent distributions of silt-clay, sand and OC (Acquavita et al., 2012a, Supplemental materials, Table S1), respectively. Initial conditions in water components were obtained by running the model for 21 years under a cyclically repeating 3-year time series of the boundary conditions, and by letting the model adjust to such external forcing to achieve a pseudo-stable condition. This adjustment is usually referred to as model spin-up.

We performed 3-year simulations after the spin up. The hydrodynamic model was forced by actual data of tidal levels at the inlets, river discharge data, wind forcing and thermal fluxes. Actual meteorological data (i.e., daily light intensity, daylight hours, monthly water temperature and average air temperature; see Supplemental materials, Table S1) were used as external forcing for biogeochemical processes such as organic solid production and degradation, photoreactions and microbial transformations of Hg species. All of the forcing data refer to data obtained during 2009–2011 and were provided by ARPA-FVG.

The time course of  $Hg_D$  concentration at the inlets was prescribed in agreement with monthly measurements (see Supplemental materials and Table S1), and the time series of  $Hg_T$  concentrations (not measured) were estimated by multiplying the  $Hg_D$  time series by a correction factor of 1.5 that was derived from experimental information on the  $Hg_T/Hg_D$  in the Gulf of Trieste (Faganeli et al., 2014, see Supplemental materials, Table S1). As a safety measure, we verified that the average values of the reconstructed  $Hg_T$  series were in agreement with the values reported by Horvat et al. (2003) and Faganeli et al. (2003) for the Gulf of Trieste (Supplemental materials, Table S1). No information on the seasonal dynamics of MeHg at the sea boundaries was available, so we adopted the constant value of 0.22 pM used by Horvat et al. (2003) for the Gulf of Trieste. Monthly values of particulate organic matter (POM) in the northern Adriatic Sea were prescribed at the sea boundaries.

Hg inputs from the Stella and Natissa rivers were estimated using measured time series of  $Hg_D$  (ARPAFVG, Supplemental materials, Table S1), and by assuming that  $Hg_D$  was 60% of  $Hg_T$ ; these values were in accordance with previous studies on the Aussa–Corno river (Covelli et al., 2009), and literature on similar rivers (Sharif et al., 2014; Buckman et al., 2015). We also estimated MeHg in the river to be 5% of  $Hg_T$ , in accordance with previous studies on temperate rivers (Balogh et al., 2003; Paller et al., 2004; Sharif et al., 2014). The concentrations of  $Hg^0$  at the atmospheric boundary were set conservatively and were equal to the average value of total gaseous Hg (TGM) measured in the lagoon watershed (Acquavita et al., 2012b). Deposition of Hg over the surface of the lagoon was treated as an external input, and the average deposition rate ( $kg/m^2$ ) was set using estimates from Žagar et al. (2007) for the Mediterranean Sea (Supplemental materials, Table S2).

The SPM concentration at the river boundaries was given by ARPAFVG measurements at the Aussa–Corno River. The POM concentration in the river boundary was calculated from available monthly SPM data (Supplemental materials, Table S1) according to Covelli et al., 2009 and Sutherland, 1998, assuming the POM fraction was 12.7% of the total SPM.

### 2.3. Model setup for Hg dynamics, partition coefficients and Hg transformations

Transformation rate constants and transport coefficients were obtained from the literature on studies conducted in the Marano–Grado Lagoon, when available, or in other similar environments. The partition coefficient ( $K_D$  in L/kg) is defined as the ratio between the concentration of a substance in the solid phase and the concentration of the substance in the enveloping aqueous phase (Hammerschmidt and Fitzgerald, 2004). The WASP7 model uses  $K_D$  values constant in space and time, which were chosen according to the calibration results (Supplemental materials, Table S3) and based on values provided by Covelli et al. (2008a, 2008b) and Hines et al. (2012) for the Marano–Grado Lagoon. Methylation and demethylation rate constants in sediment were derived from seasonal values reported by Hines et al., 2012 standardized to 20 °C, according to the equations implemented in WASP7 and assuming only the dissolved fractions of Hg and MeHg were subjected to methylation and demethylation.

Because studies on photo-reactions (e.g., photo-demethylation, photo-reduction and photo-oxidation) for the Marano–Grado Lagoon water column are missing, we parameterized these processes in agreement with Monperrus et al. (2007a, 2007b) and Whalin et al. (2007). The former explored seasonal variations in methylation, demethylation, reduction rates and photo-demethylation in the Thau Lagoon and in the open Mediterranean Sea. The latter measured photo-reduction and photo-oxidation rates at different salinities and environmental conditions and investigated the occurrence of methylation and photo-demethylation in seawater (Supplemental materials, Table S2). Given the light intensity at which the reactions were measured, photo-demethylation rates were internally adjusted by the model for the light conditions of the system. We assumed that these reactions were driven by UV-A and UV-B radiation (Vost et al., 2012) and that only the DOC-complexed fractions of  $Hg^{II}$  and MeHg were prone to photo-reactions (Vost et al., 2012; Whalin et al., 2007).

The movement of Hg species from pore water to the water column depends on diffusion processes. We averaged the molecular diffusion coefficients ( $D_t$  in m/s) for Hg and MeHg at 25 °C and adjusted the value to the water temperature of each box, according to Rothenberg et al. (2008) (Supplemental materials, Table S2). Bioturbation was then taken into account by increasing the  $D_t$  10 times from May to September to accommodate more intense biological activity. The average  $D_t$  for the whole year was  $8.5 \times 10^{-9}$  m<sup>2</sup>/s and was in the acceptable range reported by Schnoor et al. (1987) for bioturbated sediments.

The biotic solid production rate (g/m<sup>3</sup>day)  $R_{pp}$  was set in agreement with Sorokin et al. (1996) and Blasutto et al. (2005) for the water boxes and for benthic boxes, respectively. The organic matter degradation rate constant  $-K_{deg-POM}$  (1/day) was calibrated to match US EPA (1995) values. Sediment deposition, erosion and burial were computed by the model depending on the value of the shear stress induced by the currents. Average values of deposition and resuspension rates were 1.3 m/day and  $9.6 \times 10^{-7}$  m/day (corresponding to  $1.22 \times 10^3$  g/m<sup>2</sup>y and  $3.78 \times 10^2$  g/m<sup>2</sup>y of settled and resuspended particles), respectively, which is in agreement with the value of the resuspension rate of  $4.21 \times 10^2$  g/m<sup>2</sup>y given by Bloom et al. (2004) for the southern basin of the Venice Lagoon. The highest value of the modeled resuspension rate was  $2.79 \times 10^{-4}$  g/m<sup>2</sup>s, which was lower than the rates measured by Brand et al. (2010) in the South San Francisco Bay. The average burial rate was 0.11 g/cm<sup>2</sup>y and was comparable to the rates estimated in three stations of the Marano–Grado lagoon by Covelli et al., 2012.

## 3. Results and discussion

### 3.1. Model estimates and model-data comparison

The model output was compared with an independent data set of  $Hg_D$  in the Marano–Grado Lagoon water (ARPAFVG, Table S2) and

MeHg in sediment (Acquavita et al., 2012a, Supplemental materials, Table S1). We compared the WASP7 model output of each box with the average, minimum and maximum concentrations of  $Hg_D$  in the corresponding months and at the corresponding sampling stations (Fig. 4A, Table 5). The model was able to reproduce temporal variability throughout the year and spatial variability between the boxes. However, spatial variability was underestimated. The misfit, computed from the monthly values of all the boxes, was 34% which is a rather good result for this type of model, especially given the complexity of the phenomena described. A closer analysis of the data-model comparison indicated that a large fraction of the misfit was related to the months of September and November. Without these values, the fit would have improved significantly. We suspect the inconsistency between the model and field data for these months is due to the low resolution of the field data, which was collected once each month and may not be representative of average conditions; importantly, these data could also reflect the occurrence of atypical 25 events. Conversely, the boundary conditions which drove the model referred to typical average conditions. Incidentally, this is why all models typically underestimate observed variabilities.

Finally, the description of the domain did not take into account some of the local processes that affected the dynamics of the Hg species, including local tidal oscillations, desorption induced by changeable redox conditions and other effects induced by variable bathymetry such as variable thermal inertia. Several authors (Bloom et al., 2004; Bouchet et al., 2013; Guédron et al., 2012) reported substantial variations of Hg species concentrations due to the effects of tidal movements. Bloom et al. (2004) found that  $Hg_T$  in the water column of a channel of the Venice Lagoon was inversely correlated with tide height, while MeHg varied only slightly. Again in the Venice Lagoon, Guédron et al. (2012) found increased Me $Hg_D$  and  $Hg_D$  levels at the sediment–water interface and, to a lesser extent, in the water column during late tidal flooding. The authors concluded that in Venice, the release of dissolved Hg species from the salt marshes during tidal flushing affected Hg concentrations in the water column. Tidal flooding enhances shear stress along the lagoon sediments, which, in turn, could cause oxygen penetration and redox oscillations leading to enhanced Me $Hg_D$  and  $Hg_D$  release from sediments by promoting diffusion and MeHg production. Bouchet et al. (2013) found Me $Hg_D$  and  $Hg_D$  levels in a channel of the Arcachon Bay to be related to tidal movements and turbidity peaks, with maxima recorded during ebb tide.

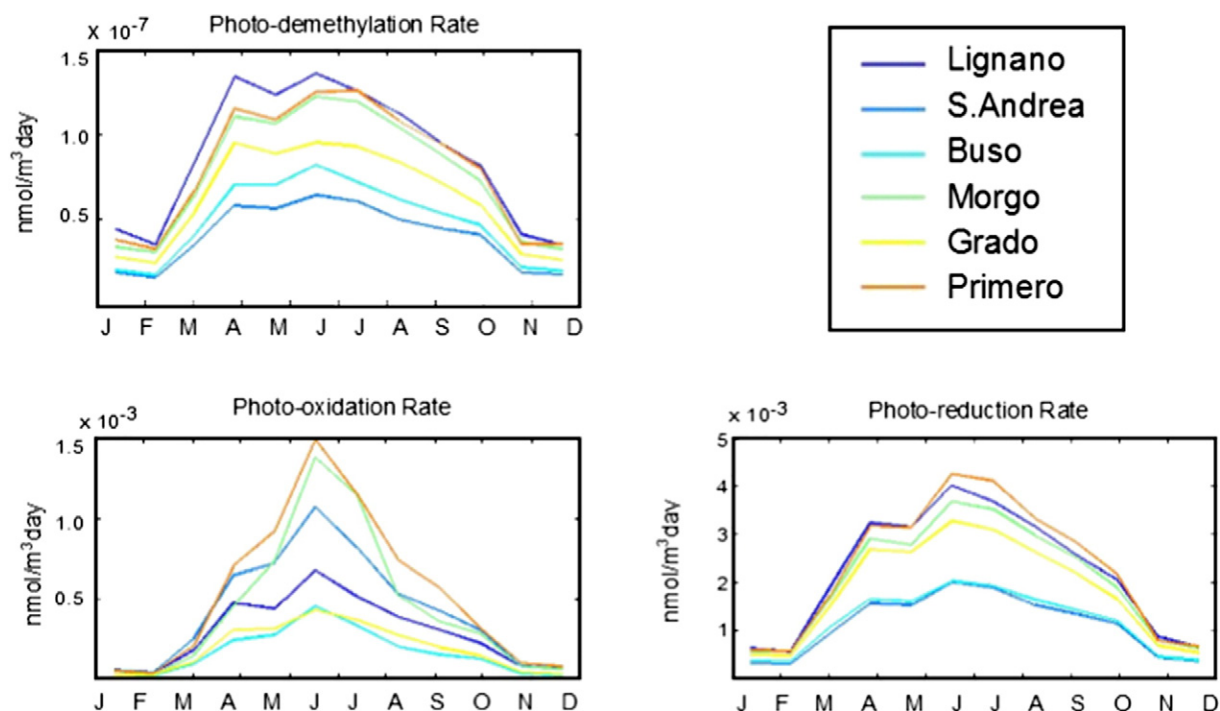
In the model, Hg transformation rates change with time and depend on temperature, solar radiation, and water fluxes. For example, Fig. 3 shows that over the course of a year, the methylation, demethylation, photo-reduction, photo-oxidation and photo-demethylation processes for the 6 sub-basins exhibits temporal variation which we attribute to seasonal fluctuations in the parameters that influence Hg transformations. Therefore, net fluxes between Hg species vary accordingly in space and in time, depending on Hg concentration and transformation rates.

The modeled Marano–Grado Lagoon surface sediment Me $Hg_p$  contents averaged 15.4 pmol/g, which was in satisfactory agreement with the average measured concentration of 13.6 pmol/g (Acquavita et al., 2012a) as shown in detail for each box in Fig. 4B. Agreements with experimental estimates varied in space and were extremely good for the Buso sub-basin; the Grado sub-basin had a larger, but still acceptable, misfit. The differences, however, point to the need for more accurate information on the spatial variability of methylation and demethylation constants (currently measurements refer to only 4 points, none of which are within the Grado subbasin; Hines et al., 2012), and possibly on the relationships between methylation rates and sediment properties or biological substrata.

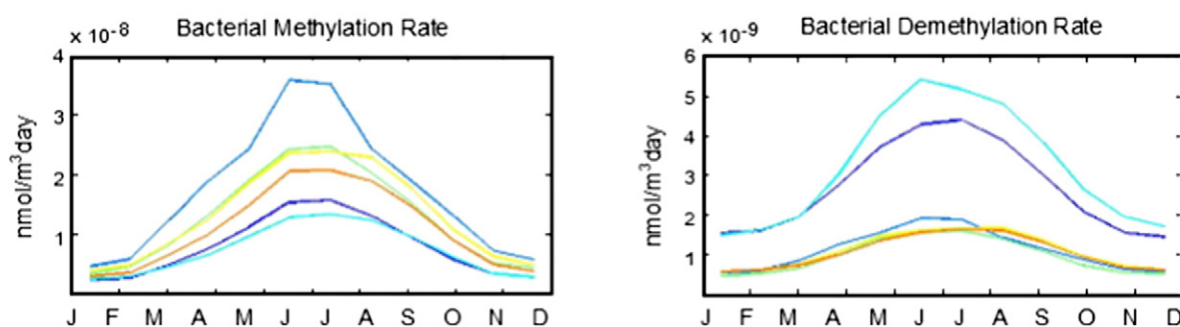
### 3.2. Hg budget in the Marano–Grado Lagoon

The model provides an estimate of three Hg species ( $Hg_T$ , MeHg and  $Hg^0$ ) concentrations and fluxes in the water column and sediment of the

## Modeled transformations in the water



## Modeled transformations in the sediment



**Fig. 3.** Time evolution of photo-demethylation, photo-oxidation, photo-reduction, methylation and demethylation, rates modulated by the model during the three years, as a function of the environmental parameters.

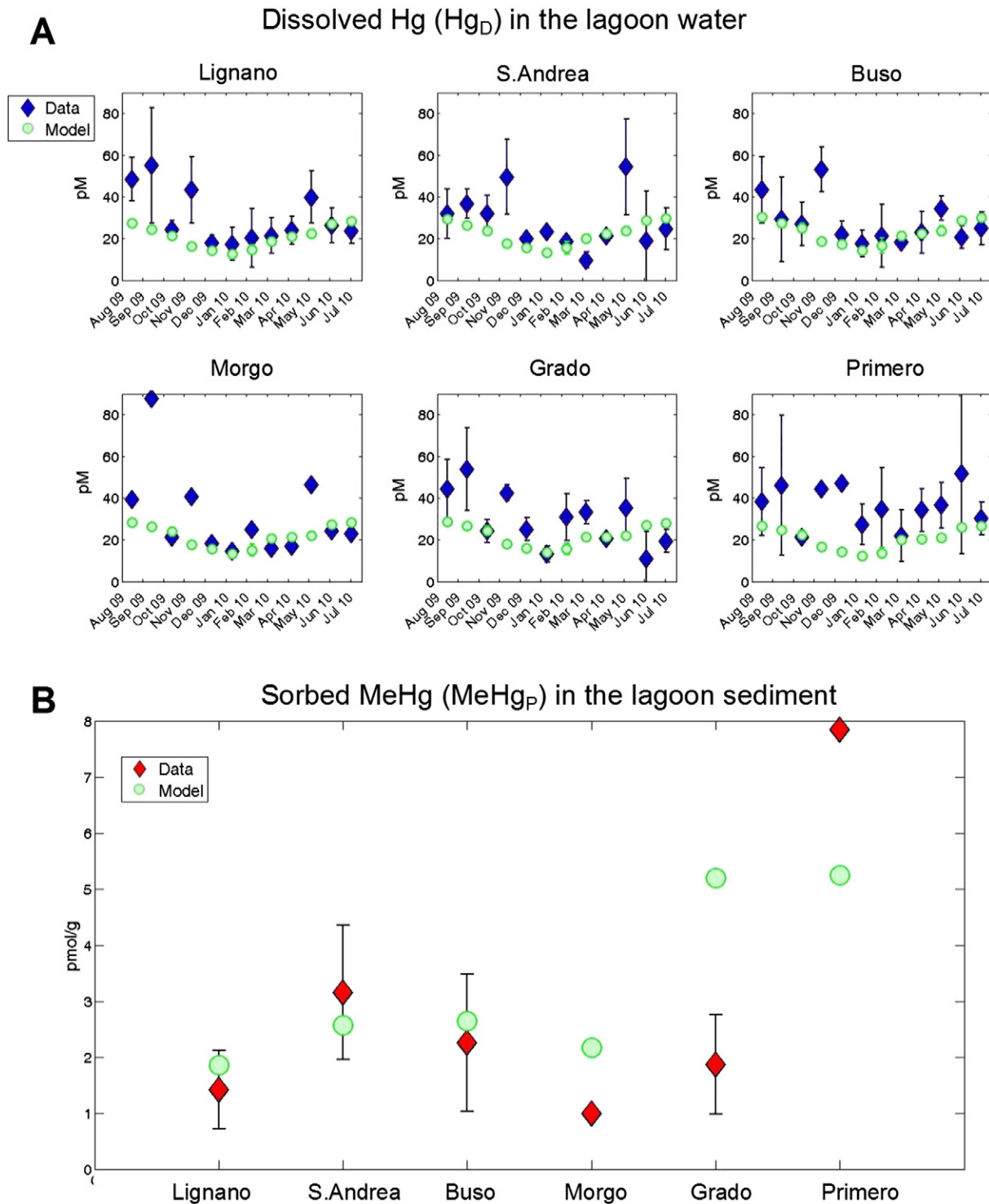
Marano–Grado Lagoon in a 21 box representation. The advantage of the model application lays in its ability to reproduce the Hg dynamics of the system at each time step, and as a function of environmental variables (i.e., water and air temperatures, light intensity, sediment resuspension, water fluxes, organic matter). This offers an advantage over purely statistical analyses of environmental measurements. Furthermore, the model allows the user to quantify the exchanges among sub-basins and with the adjoining systems (Adriatic Sea, rivers, atmosphere), a process that is difficult to assess through direct measurements.

The model was used to compute the mass balance of Hg in the Marano–Grado Lagoon, considering time-variable river loads, exchanges with the Adriatic Sea, atmospheric deposition, the initial sediment  $\text{Hg}_T$  content and  $\text{Hg}_S$  fraction. Modeled fluxes between environmental compartments of total Hg ( $\text{Hg}_T$ ), total MeHg ( $\text{MeHg}_T$ ),  $\text{Hg}^0$ , particulate Hg ( $\text{Hg}_P$ ) and MeHg ( $\text{MeHg}_P$ ) as well as dissolved Hg ( $\text{Hg}_D$ ,  $<0.45 \mu\text{m}$ ) and MeHg ( $\text{MeHg}_D$ ) are shown in Fig. 5A, together with the average concentration of each compartment. Similar information for each sub-basin is reported in Table 1. Finally, the net exchanges of  $\text{Hg}_T$  and  $\text{MeHg}_T$  between

the 6 lagoon boxes and between each box and the sea are reported in Fig. 5B.

The simulated average  $\text{Hg}_T$  concentration in the water column was 39 pM, while  $\text{Hg}^0$  was 0.3 pM (approximately 0.7% of  $\text{Hg}_T$ ) and  $\text{MeHg}_T$  was 0.25 pM (0.6% of  $\text{Hg}_T$ ). This indicates that the lagoon water concentrations of  $\text{Hg}_T$  and MeHg were 11% and 13% higher than the concentrations in incoming water from the Adriatic Sea, respectively.  $\text{Hg}_T$  and MeHg concentrations in the water column were slightly higher in the Marano Lagoon (40 and 0.26 pM) compared to the Grado Lagoon (38 and 0.23 pM), while  $\text{Hg}^0$  was higher in the Grado Lagoon (0.32 pM) than in the Marano Lagoon (0.27 pM). Model estimates of  $\text{Hg}^0$  and MeHg were coherent with the experimental findings in Emili et al. (2012).

The model predicted that water column  $\text{Hg}_T$  and MeHg occurred primarily in the dissolved phase. Dissolved ( $<0.45 \mu\text{m}$ )  $\text{Hg}_T$  and MeHg comprised 57% and 62% of the total concentration, respectively. These ratios were similar to those reported for the Thau Lagoon (Monperrus et al., 2007a, 2007b), where  $\text{Hg}_D$  ranged from 61 to 81% and  $\text{MeHg}_D$



**Fig. 4.** A) Comparison between modeled (green circle) and observed (blue diamonds) dissolved Hg ( $Hg_D > 0.45 \mu m$ ) concentrations in the lagoon water for the six sub-basins in each month. B) Comparison between modeled (green circle) and observed (red diamonds) sorbed MeHg ( $MeHg_P$ ) concentrations in the lagoon sediment for the six sub-basins.

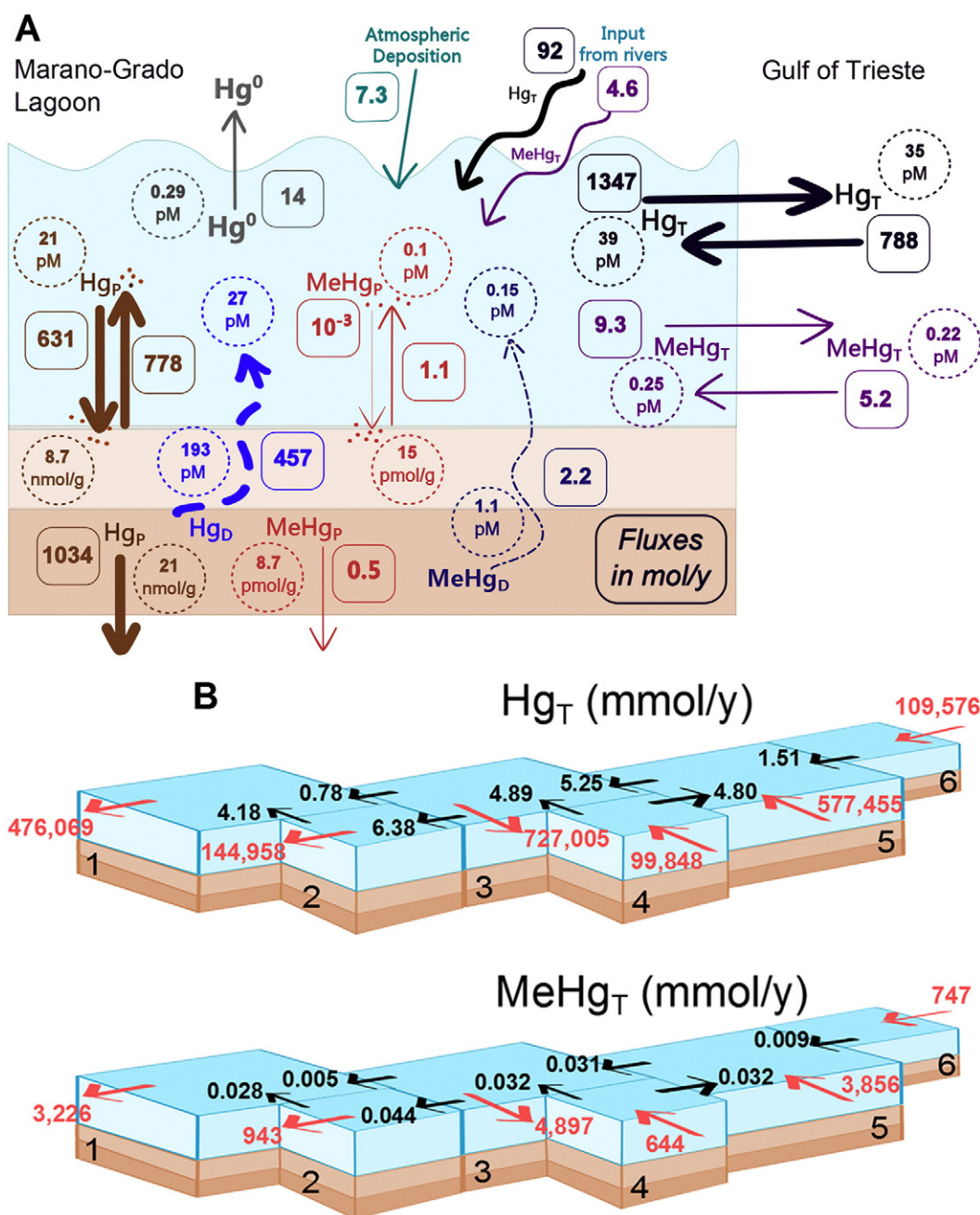
from 52 to 74%. The ratios were also comparable with the data of the Gulf of Trieste (mean  $Hg_D$  is 42%, range 6–90%; Faganeli et al., 2003). In contrast, the ratios were much higher than those reported for the Venice Lagoon by Bloom et al. (2004), where  $Hg_D$  was 15% on average (range 4–39%) and  $MeHg_D$  was 35% (range 23–56%). These discrepancies may be due to high resuspension levels of contaminated sediment in Venice.

The model predicts that the lagoon is a net source of Hg species for the Adriatic Sea, exporting 559 mol/y of  $Hg_T$  of which 4.1 mol/y is

MeHg. The percentage of MeHg (0.73%) is comparable to the average values reported in Venice Lagoon (0.65%, Bloom et al., 2004), which is another site that is heavily impacted by direct industrial pollution. Approximately 788 mol/y of  $Hg_T$  and 5.2 mol/y of  $MeHg_T$  enters the lagoon from the eastern inlets (Primero, Grado, Morgo) and 1347 mol/y of  $Hg_T$  and 9.3 mol/y of  $MeHg_T$  exit from the western inlets (Buso, S. Andrea, Lignano).

In agreement with our calculations,  $Hg_T$  export from the Marano–Grado Lagoon is higher than the export from other contamination hot





**Fig. 5.** A) Modeled concentrations (circles) and fluxes (squares) of Hg species in the Marano–Grado Lagoon.  $Hg_T$  is total Hg ( $Hg^{II} + Hg^0 + MeHg$  in dissolved and particulate phase),  $MeHg_T$  is total MeHg (dissolved and particulate phases of MeHg),  $Hg_P$  and  $MeHg_P$  are particulate-bounded  $Hg^{II}$  and MeHg, whilst  $Hg_D$  and  $MeHg_D$  are the dissolved phases of  $Hg^{II}$  and MeHg. All fluxes are in mol/y and the width of the arrows is proportional to the square root of the magnitude of the flux. B) 3D framework of the modeled lagoon, net exchanges of  $Hg_T$  and  $MeHg_T$  between the boxes of the lagoon (black arrows) and between each box and the sea (red arrows). All fluxes are in mmol/y.

spots such as the Augusta basin (159 mol/y – Sprovieri et al., 2011) and the Aveiro Lagoon (209–383 mol/y, Pereira et al., 2009). Our estimation of Hg export is one order of magnitude less than that provided by Bloom et al. (2004) for the Venice lagoon (5533 mol/y exported to the Adriatic Sea). However, caution should be taken when comparing budgets obtained with different methods because this may lead to incorrect conclusions. In fact, Hg budgets are sometimes given as a first order assessment, in which time dynamics are not considered and fluxes are computed simply as the product of average concentrations and time average exit/enter volume flows without considering mixing processes and concentration variations in time. (Bloom et al., 2004; Pereira et al., 2009 and Sprovieri et al., 2011). Furthermore, some budget

measurements only refer to a part of a larger system or to a period of the year and are then extrapolated to the whole, again neglecting space and time variability. In other cases, different assumptions or limited data sets are used. As an example, Melaku Canu et al. (2012), used a simplified physical representation of the system and only assessed the  $Hg_D$  fraction of the Hg budget. Oversimplification of the data occurs frequently, which surely affects final assessments and emphasizes the need of great caution in comparison exercises.

Other output terms in our budget are the evasion of  $Hg^0$  toward the atmosphere and the burial of contaminated sediments. Modeled volatilization of  $Hg^0$  from the water column represented a loss term of 14 mol/y, corresponding to an average evasion rate equal to  $0.098 \mu\text{mol}/\text{m}^2\text{y}$ ,



**Table 1**  
Model estimates of mercury cycle fluxes for the six sub-basins and for the total lagoon under reference conditions. All fluxes are given in mol/y. The last columns report changes in fluxes for the total lagoon under the two additional scenarios obtained by decreasing (DB) or increasing (IB) Hg concentration at the marine boundaries. Numbers and letters related to processes are the same as in Fig. 2. Numbers in bold refer to the whole lagoon.

Sub-basin		Lignano	S.Andrea	Buso	Morgo	Grado	Primero	Total	DB (–30%)	IB (+100%)
Surface [m <sup>2</sup> ]		$5.1 \times 10^7$	$2.2 \times 10^7$	$3.6 \times 10^7$	$2.9 \times 10^6$	$3.3 \times 10^7$	$1.4 \times 10^7$	<b><math>1.6 \times 10^8</math></b>		
1 – Exchange with the sea	Hg <sub>T</sub>	–475	–145	–727	100	578	110	–559	–1.39%	+4.06%
	MeHg <sub>T</sub>	–3.30	–0.97	–5.02	0.64	3.81	0.74	–4.1	–0.18%	+0.53%
2 – Input from rivers	Hg <sub>T</sub>	23.7	–	68.5	–	0.09	–	<b>92</b>	–	–
	MeHg <sub>T</sub>	1.18	–	3.43	–	$4 \times 10^{-3}$	–	<b>4.6</b>	–	–
3 – Atmospheric deposition	Hg <sub>T</sub>	2.34	0.99	1.64	0.14	1.53	0.63	<b>7.3</b>	–	–
4 – Volatilization	Hg <sup>0</sup>	4.02	2.84	3.66	0.37	3.51	1.90	<b>14</b>	–20.9%	+68.2%
5 – Deposition	Hg <sub>P</sub>	149	138	132	61.4	124	151	<b>631</b>	–29.5%	+88.3%
	MeHg <sub>P</sub>	$3 \times 10^{-4}$	$1.4 \times 10^{-4}$	$3 \times 10^{-4}$	$2 \times 10^{-5}$	$2 \times 10^{-4}$	$7 \times 10^{-5}$	<b><math>1 \times 10^{-3}</math></b>	–0.01%	–
6 – Resuspension	Hg <sub>P</sub>	145.05	29.55	351.15	0.01	251.97	10.28	<b>778</b>	–1.99%	+5.92%
	MeHg <sub>P</sub>	0.22	0.10	0.35	0.00	0.39	0.02	<b>1.1</b>	–1.18%	+3.50%
7 – Pore water diffusion	Hg <sub>D</sub>	–93.87	–31.59	–119	–4.39	–154	–57.6	–457	–1.41%	+4.23%
	MeHg <sub>D</sub>	–0.37	–0.28	–0.37	–0.04	–0.80	–0.35	–2.2	–1.50%	+4.53%
8 – Burial	Hg <sub>P</sub>	–	207	–	93.9	222	511	<b>1034</b>	–0.38%	+1.13%
	MeHg <sub>P</sub>	–	$1.5 \times 10^{-1}$	–	$7.3 \times 10^{-2}$	$6.8 \times 10^{-2}$	$2.1 \times 10^{-1}$	<b>0.5</b>	–0.77%	+2.30%
a – Photo-oxidation		2.44	2.52	1.57	0.22	1.12	1.30	<b>7.9</b>	–21.0%	+68.9%
b – Photo-reduction		33.1	12.4	21.2	1.92	19.9	10.4	<b>83</b>	–28.2%	+84.5%
c – Photo-demethylation		$1 \times 10^{-3}$	$4 \times 10^{-4}$	$7 \times 10^{-4}$	$1 \times 10^{-4}$	$6 \times 10^{-4}$	$3 \times 10^{-4}$	<b><math>3 \times 10^{-3}</math></b>	–	–
d – Methylation		0.71	0.68	1.24	0.10	1.61	0.77	<b>5.06</b>	–1.45%	+4.36%
e – Demethylation		0.04	0.03	0.05	0.00	0.04	0.02	<b>0.18</b>	–0.76%	+2.60%

which was comparable with the rates reported for the Adriatic Sea (Andersson et al., 2007). The figure was comparable with, but lower than, the rates measured in the heavily polluted Augusta basin (mean in June:  $0.52 \mu\text{mol}/\text{m}^2\text{y}$ , range 0.31–0.78 and mean in November:  $1.74 \mu\text{mol}/\text{m}^2\text{y}$ , range 0.62–3.14; Bagnato et al., 2013). The average volatilization rate was slightly higher in the Grado Lagoon ( $0.1 \mu\text{mol}/\text{m}^2\text{y}$ ) than in the Marano Lagoon ( $0.09 \mu\text{mol}/\text{m}^2\text{y}$ ), but the total amount of evaded Hg<sup>0</sup> was higher in the latter (9.1 vs 4.9 mol/y) due its greater surface area.

Our results suggest that the major pathways for the natural attenuation of Hg<sub>T</sub> concentrations in Marano–Grado Lagoon sediment are burial (1 kmol/y) and diffusion from the sediment to the water column (457 mol/y, of which 0.48% is MeHg). MeHg tends to move from sediment mainly via pore water diffusion (2.2 mol/y) and resuspension of MeHg<sub>P</sub> (1.1 mol/y). Both burial and diffusion processes are more intense in the Grado Lagoon relative to the Marano Lagoon, while resuspension is higher in the Marano Lagoon mainly due to differences in morphological and hydrodynamic features of the two lagoon systems. Indeed, the more intense circulation of water in the Marano Lagoon favors resuspension, while the shallower Grado Lagoon experiences accumulation of the sediment and slow release from pore water. The amount of Hg<sub>P</sub> and MeHg<sub>P</sub> buried is equal to 206 mol/y and 0.15 mol/y in the Marano Lagoon, respectively, and 825 mol/y and 0.34 mol/y in the Grado Lagoon, respectively. The annual export of Hg<sub>D</sub> and MeHg<sub>D</sub> diffusing from the pore water is, 243 and 1 mol/y in the Marano Lagoon, respectively, and 214 and 1.2 mol/y in the Grado Lagoon, respectively. These correspond to diffusion rates of  $2.2 \mu\text{mol}/\text{m}^2\text{y}$  for Hg<sub>D</sub>, and  $0.01 \mu\text{mol}/\text{m}^2\text{y}$  for MeHg in the Marano Lagoon, and diffusion rates of  $3.4 \mu\text{mol}/\text{m}^2\text{y}$  for Hg<sub>D</sub> and  $0.02 \mu\text{mol}/\text{m}^2\text{y}$  for MeHg in the Grado Lagoon. Modeled diffusion rates of pore water are lower than the estimates provided by Emili et al. (2012) based on seasonal benthic fluxes in the Marano–Grado lagoon. The authors calculated average Hg<sub>T</sub> fluxes to be  $8.4 \mu\text{mol}/\text{m}^2\text{y}$  (for the Marano Lagoon) and  $19.9 \mu\text{mol}/\text{m}^2\text{y}$  (for the Grado Lagoon, Primero station) and MeHg fluxes to be 0.23 (for the Marano Lagoon) and  $0.84 \mu\text{mol}/\text{m}^2\text{y}$  (for the Grado Lagoon, Primero station). Intense Hg transformations occurred in water, with 83 mol/y of Hg<sup>0</sup> produced by photo-reduction and 7.9 mol/y of Hg<sup>II</sup> produced by photo-oxidation.

Due to the higher sediment concentrations of Hg<sub>D</sub> compared to MeHg<sub>D</sub> (193 vs 1.1 pM), the model computed a net production of MeHg

via microbial methylation. Approximately 0.2 mol/y of Hg<sub>D</sub> was produced by demethylation and 5 mol/y of MeHg<sub>D</sub> was produced by methylation. More than half of the MeHg produced in the sediment moved to the water as a consequence of pore water diffusion (2.2 mol/y) and resuspension of the particle-bound fraction (1.1 mol/y). Approximately 10% of the MeHg produced each year was buried (0.5 mol/y), and only a small amount was reduced to Hg<sup>0</sup> by photo-demethylation (0.003 mol/y). The remaining amount of MeHg (1.2 mol/y), together with the MeHg coming from riverine sources (4.6 mol/y), was partially exported to the Adriatic Sea (4.1 mol/y) or remained in the lagoon water (1.7 mol/y).

An analysis of additional simulations performed after changing model Hg concentrations at the boundary enabled us to assess the sensitivity of model outputs to changes in the marine boundary. This type of assessment is usually used to assess the robustness of model results, to understand the relationships between input and output variables in a complex system, or to indicate focus areas for future measurement efforts. Melaku Canu et al. (2012) already showed that the Hg cycle in the Marano–Grado Lagoon is a little sensitive to riverine input, because there are other 2 sources of Hg which are more important, namely the Hg exchanged at the inlets (i.e. input from the sea) and the Hg exchanged at the sediment/water interface (i.e. input from the sediment). The most important input is the input from the sea, possibly because: a) the Hg concentration in sea water is anomalously high, because of the impact of the Soča/Isonzo River; b) the water volume exchanged at the inlets is higher than the water mass that comes from the rivers. In fact, the time required by the river flow to flush the entire lagoon is around 30 days, while the flushing time computed considering both the river inputs and the inlets exchanges is about 7 days.

Here we explored the model response, in terms of Hg species concentrations and overall budgets, to two hypothetical scenarios in which Hg<sub>T</sub> concentrations at the lagoon inlets were significantly higher or lower. The results indicated that a hypothetical doubling (+100%) of Hg concentration at the marine boundary would induce an average increase of Hg<sub>T</sub> and Hg<sup>0</sup> in the lagoon water by 80% and 70%, respectively, a 12% increase of Hg<sub>T</sub> in the sediment compartment, and a negligible increase of MeHg and MeHg<sub>P</sub> in water. Conversely, a sharp decrease (–30%) in the Hg concentration at the marine boundary would cause a decrease of 20% of Hg<sub>T</sub> and Hg<sup>0</sup> in the lagoon water and a decrease of 3% of Hg<sub>T</sub> in the sediment compartment. Accordingly, the evasion flux would increase by 68% (or decrease of 21%) with an increase (or decrease) in concentration. The

export flux to the sea was less sensitive to changes in  $Hg_T$  and  $Hg^0$  concentrations at the marine boundary and varied by  $-1.4\%$ , and  $+4\%$  in the increasing and decreasing scenarios, respectively. Therefore, an increase in Hg concentration at the inlets would generally increase the Hg fluxes, but the responses are not linear and some processes are likely to be more affected than others. In particular, an estimation of the Marano–Grado Lagoon's contribution to the Hg input of the Mediterranean Sea is only slightly affected by changes in the marine boundary concentration. This result also adds robustness to our estimates.

In addition to the budget quantification, another important output of this application lies in its ability to suggest knowledge gaps that need to be addressed to reduce the level of uncertainty of the model responses, and, in particular to address future field works efforts. Current legislation mainly focuses on assessments of  $Hg_T$ , due to analytical challenges in Hg speciation measurements. However, a complete synoptic set of Hg measures of  $Hg_D$ ,  $Hg_P$ , and MeHg in water, even if maintained for a limited time period, would provide useful information to assess the performance of models and to calibrate the model for use in planning and evaluating environmental management scenarios. Moreover, MeHg measures in water would also be needed considering that these species are of major interest due to public and ecosystem health concerns. Additionally, special efforts should be made to assess photo-transformation rates such as of photo-reduction, photo-oxidation and photo-demethylation.

#### 4. Conclusion

Models, such as the one developed and presented in this study, are valuable tools that link a plethora of disconnected field studies and enable investigations on system behaviors. In this application, a model was used to assess Hg export to the Mediterranean Sea. However, this model could be used to investigate other aspects, too, such as long-term responses to environmental changes related to long-term climate variations, land use changes or morphological changes that could alter lagoon dynamics. The model has room for improvement, for instance, in aspects such as increases in spatial resolution that would allow for a better representation of spatial variability. This would require, concurrently, the availability of additional measures. Another aspect that deserves further investigation and effort is the representation of dynamics at the sediment layer, and, in particular, the dynamic modeling of the relationship between organic matter re-mineralization and  $Hg_D$  release to pore water, and the implementation of empirical diffusion functions. Sediment processes are very important in shallow water environments and play an especially crucial role in MeHg budgets.

This work provides a first comprehensive overview of the Hg cycle in the Marano–Grado Lagoon, by integrating Hg data and other environmental parameters with literature values of Hg kinetic processes into a model framework specifically developed for Hg modeling. The model was able to reproduce the average measured  $Hg_T$  and MeHg values and was used to quantify the Hg budgets between the Marano–Grado Lagoon and its surrounding environments. During its residence in the Marano–Grado Lagoon, Hg underwent several transformations, which led to a net MeHg production of  $5 \text{ mol/y}$  ( $1 \text{ kg/y}$ ) within the sediment compartment.

The estimated net export of  $Hg_T$  from the Lagoon to the Adriatic Sea was  $0.56 \text{ kmol/y}$  (i.e., approximately  $115 \text{ kg/y}$ ) for  $Hg_T$ , and  $4.1 \text{ mol/year}$  for MeHg. The  $Hg_T$  export corresponded to almost 6% of the  $Hg_T$  load to the Mediterranean basin ( $10 \text{ kmol/y}$ ) estimated by Rajar et al. (2007), thus confirming that the Marano–Grado Lagoon is an important source of Hg for the Mediterranean Sea. Results also demonstrated that the Marano–Grado Lagoon was a net emitter of  $Hg^0$  to the atmosphere. Information on Hg inputs to the Adriatic and to the atmosphere therefore appears to be crucial when assessing Hg budgets at a regional scale. Finally, our results also indicated that the most critical shortcoming of the currently available data sets is the lack of complete synoptic measurements and suggest that future experimental efforts should also include information on the photo-transformation rates.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.marchem.2015.10.013>.

#### References

- Acquavita, A., Covelli, S., Emili, A., Berto, D., Faganeli, J., Giani, M., Horvat, M., Koron, N., Rampazzo, F., 2012a. Mercury in the sediments of the Marano and Grado Lagoon (northern Adriatic Sea): sources, distribution and speciation. *Estuar. Coast. Shelf Sci.* 113, 20–31.
- Acquavita, A., Grahonja, R., Mattassi, G., Skert, N., 2012b. Biomonitoraggio di mercurio aerodisperso tramite licheni come bioaccumulatori nella Laguna di Marano e Grado e basso bacino scolante. XXV Convegno della Società Lichenologica Italiana, Roma (3–5 Ottobre).
- Amos, H.M., Jacob, D.J., Kocman, D., Horowitz, H.M., Zhang, Y., Dutkiewicz, S., Horvat, M., Corbitt, E.S., Krabbenhoft, D.P., Sunderland, E.M., 2014. Global biogeochemical implications of mercury discharges from rivers and sediment burial. *Environ. Sci. Technol.* 48, 9514–9522.
- Andersson, M.E., Gärdfeldt, 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. *Mar. Chem.* 104, 214–226.
- Bagnato, E., Sprovieri, M., Barra, M., Bitetto, M., Bonsignore, M., Calabrese, S., Di Stefano, V., Oliveri, E., Parello, F., Mazzola, S., 2013. The sea–air exchange of mercury (Hg) in the marine boundary layer of the Augusta basin (southern Italy): concentrations and evasion flux. *Chemosphere* 93, 2024–2032.
- Balogh, S.J., Huang, Y., Offerman, H.J., Meyer, M.L., Johnson, D.K., 2003. Methylmercury in rivers draining cultivated watersheds. *Sci. Total Environ.* 304, 305–313.
- Black, F.J., Conaway, C.H., Flegal, R.A., 2012. Mercury in the marine environment. In: Bank, M.S. (Ed.), *Mercury in the Environment. Pattern and Process*. University of California press ed. Bank, Michel S., Berkley and Los Angeles, pp. 167–178.
- Blasutto, O., Cibic, T., De Vittor, C., Umani, S.F., 2005. Microphytobenthic primary production and sedimentary carbohydrates along salinity gradients in the Lagoons of Grado and Marano (Northern Adriatic Sea). *Hydrobiologia* 550, 47–55.
- Bloom, N.S., Moretto, L.M., Scopece, P., Ugo, P., 2004. Seasonal cycling of mercury and monomethyl mercury in the Venice Lagoon (Italy). *Mar. Chem.* 91, 85–99.
- Bouchet, S., Amouroux, D., Rodriguez-Gonzalez, P., Tessier, E., Monperrus, M., Thouzeau, G., Clavier, J., Amice, E., Deborde, J., Bujan, S., Grall, J., Anschutz, P., 2013. MMHg production and export from intertidal sediments to the water column of a tidal lagoon (Arcachon Bay, France). *Biogeochemistry* 114, 341–358.
- Bramabati, A., 1996. *Metalli Pesanti Nelle Lagune Di Marano e Grado*. Regione Autonoma Friuli-Venezia Giulia, Trieste.
- Brand, A., Lacy, J.R., Hsu, K., Hoover, D., Gladding, S., Stacey, M.T., 2010. Wind-enhanced resuspension in the shallow waters of South San Francisco Bay: Mechanisms and potential implications for cohesive sediment transport. *J. Geophys. Res.* 115.
- Buckman, K.L., Marvin-DiPasquale, M., Taylor, V.F., Chalmers, A., Broadley, H.J., Agee, J., Jackson, B.P., Chen, C.Y., 2015. Influence of a chlor-alkali superfund site on mercury bioaccumulation in periphyton and low-trophic level fauna. *Environ. Toxicol. Chem.* 34, 1649–1658.
- Cossa, D., Harmelin-Vivien, M., Mellon-Duval, C., Loizeau, V., Averty, B., Crochet, S., Chou, L., Cadiou, J., 2012. Influences of bioavailability, trophic position, and growth on methylmercury in hakes (*Merluccius merluccius*) from northwestern Mediterranean and northeastern Atlantic. *Environ. Sci. Technol.* 46, 4885–4893.
- 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). *Estuar. Coast. Shelf Sci.* 82, 273–284.
- Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M., 2008a. Benthic fluxes of mercury species in a lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). *Appl. Geochem.* 23, 529–546.
- Covelli, S., Faganeli, J., De Vittor, C., Predonzani, S., Acquavita, A., Horvat, M., 2008b. Benthic fluxes of mercury species in a lagoon environment (Grado Lagoon, Northern Adriatic Sea, Italy). *Appl. Geochem.* 23, 529–546.
- 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). *Estuar. Coast. Shelf Sci.* 113, 7–19.
- Covelli, S., Piani, R., Acquavita, A., Predonzani, S., Faganeli, J., 2007. Transport and dispersion of particulate Hg associated with a river plume in coastal Northern Adriatic environments. *Mar. Pollut. Bull.* 55, 436–450.
- Dizdarević, T., 2001. The influence of mercury production in Idrinja mine on the environment in the Idrinja region and over a broad area. *RMZ-Mater. Geoenviron.* 48, 56–64.
- Dorigo, L., 1965. *La Laguna di Grado e le sue foci*. Ufficio Idrografico del Magistrato della Acque 155.
- Emili, A., Acquavita, A., Koron, N., Covelli, S., Faganeli, J., Horvat, M., Žižek, S., Fajon, V., 2012. Benthic flux measurements of Hg species in a northern Adriatic lagoon environment (Marano and Grado Lagoon, Italy). *Estuar. Coast. Shelf Sci.* 113, 71–84.

- Faganeli, J., Hines, M.E., Horvat, M., Falnoga, I., Covelli, S., 2014. Methylmercury in the Gulf of Trieste (Northern Adriatic Sea): from microbial sources to seafood consumers. *Food Technol. Biotechnol.* 52 (2), 188–197.
- Faganeli, J., Horvat, M., Covelli, S., Fajon, V., Logar, M., Lipej, L., Cermelj, B., 2003. Mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea). *Sci. Total Environ.* 304, 315–326.
- Ferrarin, C., Umgieser, G., Bajo, M., Bellafiore, D., De Pascalis, F., Ghezzi, M., Mattassi, G., Scroccaro, I., 2010. Hydraulic zonation of the lagoons of Marano and Grado, Italy. A modelling approach. *Estuar. Coast. Shelf Sci.* 87, 561–572.
- Fitzgerald, W.F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of mercury. *Chem. Rev.* 107, 641–662.
- Fontolan, G., Pillon, S., Delli Quadri, F., Bezzi, A., 2007. Sediment storage at tidal inlets in northern Adriatic lagoons: ebb-tidal delta morphodynamics, conservation and sand use strategies. *Estuar. Coast. Shelf Sci.* 75, 261–277.
- 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. *Estuar. Coast. Shelf Sci.* 113, 116–125.
- Guédron, S., Hugué, L., Vignati, D.A.L., Liu, B., Gimbert, F., Ferrari, B.J.D., Zonta, R., Dominik, J., 2012. Tidal cycling of mercury and methylmercury between sediments and water column in the Venice Lagoon (Italy). *Mar. Chem.* 130–131, 1–11.
- Hammerschmidt, C.R., Fitzgerald, W.F., 2004. Geochemical controls on the production and distribution of methylmercury in near-shore marine sediments. *Environ. Sci. Technol.* 38, 1487–1495.
- Heimbürger, L.E., Cossa, D., Marty, J.C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010. Methylmercury distributions in relation to the presence of nanoandpicophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). *Geochim. Cosmochim. Acta* 74, 5549–5559.
- Heimbürger, L.E., Sonke, J.E., Cossa, D., Point, D., Lagane, C., Laffont, L., Galfond, B., Nicolaus, M., Rabe, B., van der Loeff, M.R., 2015. Shallow methylmercury production in the marginal sea ice zone of the central Arctic Ocean. *Sci. Report.* <http://dx.doi.org/10.1038/srep10318>.
- Heimbürger, L.E., Cossa, D., Thibodeau, B., Khrpounoff, A., Mas, V., Chiffolleau, J.-F., Schmidt, S., Migon, C., 2012. Natural and anthropogenic trace metals in sediments of the Ligurian Sea (Northwestern Mediterranean). *Chem. Geol.* 291 (0), 141–151.
- Hines, M.E., Poitras, E.N., Covelli, S., Faganeli, J., Emili, A., Žižek, S., Horvat, M., 2012. Mercury methylation and demethylation in Hg-contaminated lagoon sediments (Marano and Grado Lagoon, Italy). *Estuar. Coast. Shelf Sci.* 113, 85–95.
- 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. *Atmos. Environ.* 37 (Supplement 1), 93–108.
- Lehnher, I., St. Louis, V.L., Hintelmann, H., Kirk, J.L., 2011. Methylation of inorganic mercury in polar marine waters. *Nat. Geosci.* 4, 298–302.
- Mason, R.P., Choi, A.L., Fitzgerald, W.F., Hammerschmidt, C.R., Lamborg, C.H., Soerensen, A.L., Sunderland, E.M., 2012. Mercury biogeochemical cycling in the ocean and policy implications. *Environ. Res.* 119, 101–117.
- Melaku Canu, D., Acquavita, A., Knightes, C.D., Mattassi, G., Scroccaro, I., Solidoro, C., 2012. Modeling the mercury cycle in the Marano–Grado Lagoon (Italy). In: Jordan, J. (Ed.), *Models of the Ecological Hierarchy: From Molecules to the Ecosphere*, 1st Edition Elsevier, pp. 239–257.
- Merritt, K.A., Amirbahman, A., 2009. Mercury methylation dynamics in estuarine and coastal marine environments — a critical review. *Earth-Sci. Rev.* 96, 54–66.
- Monperrus, M., Tessier, E., Amouroux, D., Leynaert, A., Huonnic, P., Donard, O.F.X., 2007b. Mercury methylation, demethylation and reduction rates in coastal and marine surface waters of the Mediterranean Sea. *Mar. Chem.* 107, 49–63.
- Monperrus, M., Tessier, E., Point, D., Vidimova, K., Amouroux, D., Guyoneaud, R., Leynaert, A., Grall, J., Chauvaud, L., Thouzeau, G., Donard, O.F.X., 2007a. The biogeochemistry of mercury at the sediment–water interface in the Thau Lagoon. 2. Evaluation of mercury methylation potential in both surface sediment and the water column. *Estuar. Coast. Shelf Sci.* 72, 485–496.
- Paller, M.H., Jagoe, C.H., Bennett, H., Brant, H.A., Bowers, J.A., 2004. Influence of methylmercury from tributary streams on mercury levels in Savannah River Asiatic clams. *Sci. Total Environ.* 325, 209–219.
- Pereira, M.E., LillebÅ, A.I., Pato, P., Vãjlega, M., Coelho, J.P., Lopes, C.B., Rodrigues, S., Cachada, A., Otero, M., Pardal, M.A., Duarte, A.C., 2009. Mercury pollution in Ria de Aveiro (Portugal): a review of the system assessment. *Environ. Monit. Assess.* 155, 39–49.
- Piani, R., Covelli, S., Biester, H., 2005. Mercury contamination in Marano Lagoon (Northern Adriatic sea, Italy): source identification by analyses of Hg phases. *Appl. Geochem.* 20, 1546–1559.
- Pirastu, R., Comba, P., Conti, S., Iavarone, I., Fazzo, L., Pasetto, R., Zona, A., Crocetti, E., Ricci, P., 2014. Mortality, cancer incidence and hospital discharges. *Epidemiol. Prev.* 38.
- Rajar, R., Četina, M., Horvat, M., Žagar, D., 2007. Mass balance of mercury in the Mediterranean Sea. *Mar. Chem.* 107, 89–102.
- Rothenberg, S.E., Ambrose, R.F., Jay, J.A., 2008. Mercury cycling in surface water, pore water and sediments of Mugu Lagoon, CA, USA. *Environ. Pollut.* 154, 32–45.
- Schnoor, J.L., Sato, C., McKechnie, D., Sahoo, D., 1987. Processes, Coefficients, and Models for Simulating Toxic Organics and Heavy Metals in Surface Waters. U.S. EPA, Athens, GA (EPA/600/3–87–015).
- Sharif, A., Monperrus, M., Tessier, E., Bouchet, S., Pinaly, H., Rodriguez-Gonzalez, P., Maron, P., Amouroux, D., 2014. Fate of mercury species in the coastal plume of the Adour River estuary (Bay of Biscay, SW France). *Sci. Total Environ.* 496, 701–713.
- Soerensen, A.L., Mason, R.P., Balcom, P.H., Jacob, D.J., Zhang, Y., Kuss, J., Sunderland, E.M., 2014. Elemental mercury concentrations and fluxes in the tropical atmosphere and ocean. *Environ. Sci. Technol.* 48 (19), 11312–11319.
- Sonke, J.E., Heimbürger, L., Dommergue, A., 2013. Mercury biogeochemistry: paradigm shifts, outstanding issues and research needs. *Compt. Rendus Geosci.* 345, 213–224.
- Sorokin, Y.I., Sorokin, P.Y., Giovanardi, O., Dalla Venezia, L., 1996. Study of the ecosystem of the lagoon of Venice, with emphasis on anthropogenic impact. *Mar. Ecol. Prog. Ser.* 141, 247–261.
- Sprovieri, M., Oliveri, E., Di Leonardo, R., Romano, E., Ausili, A., Gabellini, M., Barra, M., Tranchida, G., Bellanca, A., Neri, R., Budillon, F., Saggiomo, R., Mazzola, S., Saggiomo, V., 2011. The key role played by the Augusta basin (southern Italy) in the mercury contamination of the Mediterranean Sea. *J. Environ. Monit.* 13, 1753–1760.
- Sunderland, E.M., Krabbenhoft, D.P., Moreau, J.W., Strode, S.A., Landing, W.M., 2009. Mercury sources, distribution, and bioavailability in the north Pacific Ocean: insights from data and models. *Glob. Biogeochem. Cycles* 23 (2).
- Sutherland, R., 1998. Loss-on-ignition estimates of organic matter and relationships to organic carbon in fluvial bed sediments. *Hydrobiologia* 389, 153–167.
- US EPA, 1995. Total Maximum Daily Load (TMDL) for Settleable Solid Residues in the Waters of Akutan Harbor, Alaska. Environmental Protection Agency, Seattle, WA. Region X (Appendix A).
- US EPA, 2009. Water Quality Simulation Program v. 6. manual. Wool T. A., Ambrose R. B., Martin J.L., Comer E. A.
- US EPA, 1988. Water quality Simulation program, v. 5. manual. (Ambrose R.).
- Vost, E.E., Amyot, M., O'Driscoll, N.J., 2012. Photoreactions of mercury in aquatic systems. In: Liu, G., Cai, Y., O'Driscoll, N. (Eds.), *Environmental Chemistry and Toxicology of Mercury*. Wiley ed. JOHN WILEY & SONS, INC., pp. 193–218.
- Watrass, C.J., Back, R.C., Halvorsen, S., Hudson, R.J.M., Morrison, K.A., Wente, S.P., 1998. Bioaccumulation of mercury in pelagic freshwater food webs. *Sci. Total Environ.* 219, 183–208.
- Whalin, L., Kim, E., Mason, R., 2007. Factors influencing the oxidation, reduction, methylation and demethylation of mercury species in coastal waters. *Mar. Chem.* 107, 278–294.
- Wool, T.A., Ambrose, R.B., Martin, J.L., Comer, E.A., 2001. Water Quality Analysis Simulation Program (WASP) Version 6.0: User's Manual.
- Žagar, D., Petkovšek, G., Rajar, R., Sirknik, N., Horvat, M., Voudouri, A., Kallos, G., Četina, M., 2007. Modelling of mercury transport and transformations in the water compartment of the Mediterranean Sea. *Mar. Chem.* 107, 64–88.