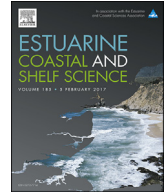




Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

journal homepage: www.elsevier.com/locate/ecss

Long-term scenarios of mercury budgeting and exports for a Mediterranean hot spot (Marano-Grado Lagoon, Adriatic Sea)

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ARTICLE INFO

Article history:

Received 1 March 2016

Received in revised form

7 October 2016

Accepted 17 December 2016

Available online xxx

Keywords:

Mercury

Modelling

Lagoon

Budget

WASP7

Scenario analysis

Sediment

Climate

ABSTRACT

The Marano-Grado Lagoon (MGL) is extensively contaminated by mercury (Hg) from local sources and long-term (500 years) tidally delivered inputs from the Idrija Hg mine (Slovenia) through Isonzo River suspended loads.

A multibox WASP-7 (Water Analysis Simulation Program) model was used to simulate the long-term dynamics of the mercury cycle in the MGL.

Scenario simulations were used to compute changes in the system over 100 years. Present and future Hg concentrations in water, sediment, and Hg budgets were compared, including evasion and MeHg inputs to the Mediterranean Sea, based on climate changes and mercury capping in tributary rivers.

Using the Ref baseline scenario, the model computes a general decrease in Hg_T of 13% in the water column and of 80% in sediment and a strong MeHg increase in sediment (+73%). The net sea export of Hg_T decreases by 57% to up to 48 kg/y while MeHg increases by 10% to up to 0.63 kg/y.

The lagoon sediment recovery time of Hg_T up to a target level of 0.3 mg/kg is computed over 570 years for surface sediments (1750 for subsurface sediments). When removing Hg from boundaries, the same target value for surface sediments is reached within 110 years.

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1. Introduction

Mercury is a persistent pollutant of global concern that can accumulate in organisms and that can have adverse health effects. Its presence is mainly a result of past human activities such as mining and industrial dumping that have severely altered the state of mercury concentrations in several transitional systems worldwide. A SCOPUS abstract search based on keywords “mercury”, “contamination”, and “estuaries” retrieved 153 papers published from 1985, 65 of which are focused on “lagoons”. The number of studied sites and their global distributions highlight the relevance of this issue also because estuarine and transitional environments play a crucial role in the production of MeHg, a central driver of mercury bioaccumulation in pelagic organisms (Balcom et al., 2015).

The quantification of mercury export contributions from coastal lagoons and estuaries is, therefore, relevant for the assessment of mercury budgets at the global and regional scales. Several budget

analysis and modelling efforts are being pursued to this end to evaluate and inter-compare Hg fluxes such as evasion fluxes (Sharif et al., 2013), transfer to food webs (Balcom et al., 2015), riverine inputs (Amos et al., 2014), and transfer to seas and oceans (Zagar et al., 2006; Pato et al., 2008; Bloom et al., 2004; Canu et al., 2012; Melaku Canu et al., 2015; Sprovieri et al., 2011).

Mathematical models are also suitable tools for addressing long-term trajectories under different conditions, including changes in boundary inputs and climate changes (Harley et al., 2006). Scenario analyses are often used to explore system trends and responses according to different assumptions based on direct and indirect effects of human interventions, explore long term trends under semi-stationary conditions (e.g., climate change effects on marine biogeochemistry (Cossarini et al., 2008; Lazzari et al., 2013; Solidoro et al., 2010) or on persistent pollutants (Dalla Valle et al., 2007)) and explore the effectiveness of management responses (Canu et al., 2010; Melaku Canu et al., 2001; Thompson and Flower, 2009).

In this work, a mercury model already formulated and tested for the Marano-Grado Lagoon (Melaku Canu et al., 2015) is used to evaluate long-term mercury contamination trends in the lagoon under alternative scenarios.

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The Marano–Grado Lagoon (Italy) is a coastal lagoon in the Mediterranean Sea (Fig. 1) of roughly 160 km² that receives freshwater inputs from rivers and marine inputs from the Northern Adriatic Sea. Tidally driven water exchange with the Adriatic Sea is bidirectional and occurs through six inlets (i.e., Lignano, S. Andrea, Buso, Morgo, Grado and Primero, Fig. 1) after which the 6 sub-basins were named (Dorigo, 1965). Riverine effects, given the strong seasonal variations in salinity, have been identified in the western section of the lagoon while the eastern section is more marine driven (Ferrarin et al., 2010).

The lagoon is a hot spot of mercury contamination (Covelli et al., 2012) as a consequence of mining and industrial activities that have caused the release of large amounts of mercury compounds into the environment. As Hg is pervasively present in the lagoon sediment, diffuse reclamation is not feasible. The historical source of Hg is the Idrija cinnabar mine (Slovenia), which has been estimated to have released 37,000 tons of Hg over 500 years of activity (Dizdarević, 2001). The Hg extraction in the Idrija mine reached a maximum at the end of the XIX century, followed by a gradual decrease in the following decades. The ore dumping in the environment followed a similar pattern, until 1970, when the direct dumping into the river was finally prohibited. At the end of the 1980's the Hg production was 1/10 of the peak's production reached in 1890. (Gnamuš and Horvat, 1999; Čar and Dizdarević, 2004). This material has been transported by the Soča-Isonzo River and delivered to the Gulf of

Trieste (Zagar et al., 2006). While most particulate Hg deposits are found close to riverbanks, prevailing currents also drive suspended and dissolved materials further south towards the Marano-Grado Lagoon. Currently, average sediment concentrations reach 721 ppm downstream from the mine (Gosar and Teršič, 2015), 40 ppm at the Soča-Isonzo River mouth (Gosar and Teršič, 2015), 1 ppm in the central Gulf of Trieste (Faganeli et al., 2014) and 4.4 ppm in the Marano-Grado Lagoon, thus ranging from 0.6 to 10 ppm (Acquavita et al., 2012). Higher levels in the sediment of the Marano-Grado Lagoon compared to those in the open Gulf of Trieste are attributable to the following different processes: 1) the direction of currents; 2) the lagoon as a more confined environment; and 3) the presence of an additional source of contamination.

In addition to inputs from the mining site, the lagoon has been receiving direct inputs of Hg through its Aussa-Corno River tributary from a former chlor-alkali plant that has dumped roughly 190 tons of Hg over 45 years (Acquavita et al., 2012). Historically, the lagoon has acted as a sink for Hg transported from the Gulf of Trieste and the chlor-alkali plant, accumulating roughly 251 tons of Hg in its sediments (Covelli et al., 2012). A mass balance study showed that under present conditions, outputs from the lagoon exceed inputs (Melaku Canu et al., 2015), and, thus, in the long-term, a natural decontamination of Hg stored in the lagoon's environmental compartment is expected. Here, we explore the time scale for the natural recovery of sediment and the relevance of

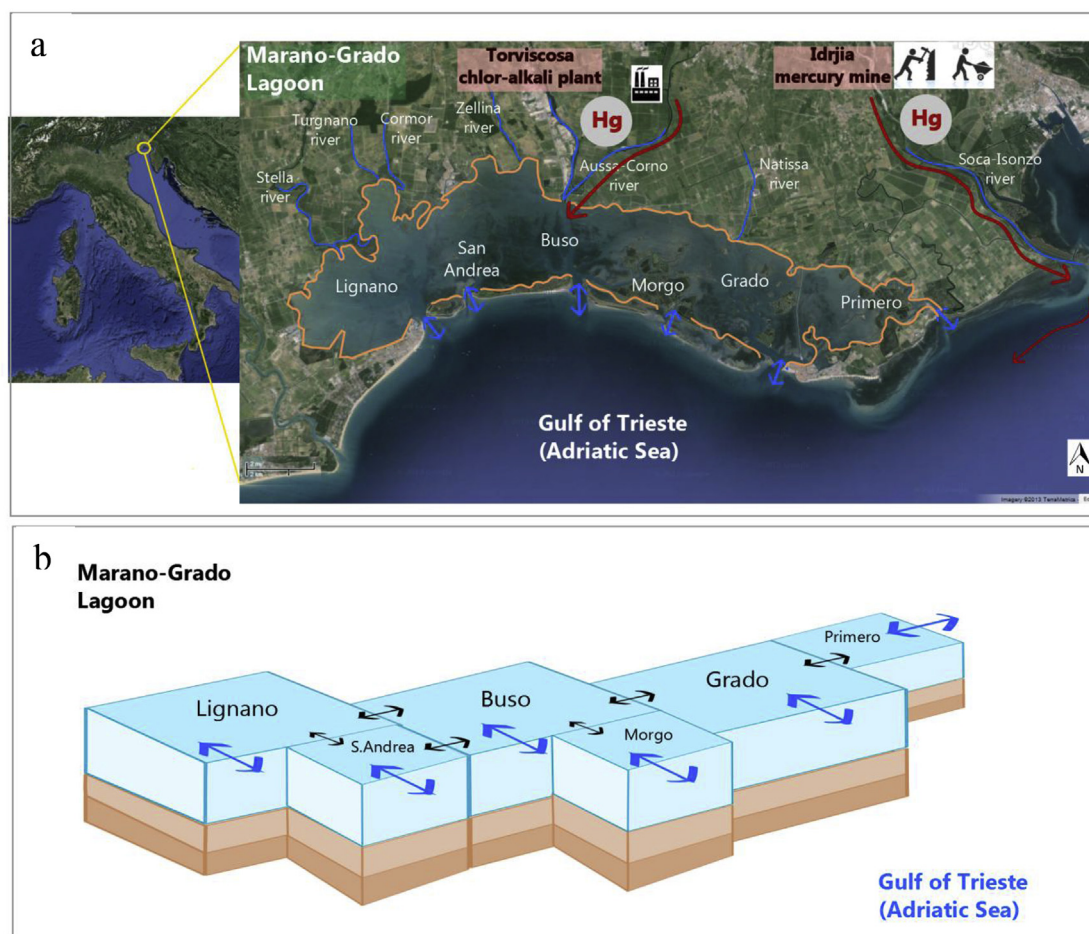


Fig. 1. a) Satellite image of the Marano-Grado Lagoon. The lagoon boundary is highlighted in orange, riverine inputs and marine exchanges are represented in blue, local anthropogenic Hg inputs are shown in red. b) box model representation of the Marano–Grado Lagoon in 6 boxes each formed by a water layer, and two sediment –surface and subsurface–layers (adapted from Melaku Canu et al., 2015). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

different inputs and forcings to mercury dynamics in the lagoon using different future scenarios to take into account effects of environmental variability and climate change projections on mercury biogeochemistry dynamics and fluxes.

2. The model structure and its application

The dynamic and spatially resolved water quality model was applied using the Water Quality Analysis Simulation Programme (WASP7, v7.3) as described in Melaku Canu et al. (2015).

As described by Wool et al. (2001), the model simulates the dynamic evolution of three mercury species over time (divalent inorganic mercury ($\text{Hg}(\text{II})$), methylmercury (MeHg) and elemental mercury (Hg^0)) and three solids types (silt, sand, and biotic solids) in a discretised box system.

The overall equation for the mass conservation of generic state variable C (representative of a mercury species) in each water box includes terms for advection (U in m/sec) and diffusion (E in m^2/day) in the three dimensions (x, y, z) and reads as Eq. (1.1). The equation also accounts for the biogeochemical transformation of Hg species (S_{rx} in $\text{g}/\text{m}^3 \text{ day}$), direct and diffusive loads (S_L in $\text{g}/\text{m}^3 \text{ day}$), and exchanges with boundaries or sediment (S_B in $\text{g}/\text{m}^3 \text{ day}$):

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

Advective and diffusive processes are responsible for the exchange of water, particles and solutes between water boxes and between boxes and their boundary systems including the atmosphere, deep sediments, and marine boundaries. While transported, Hg species are partitioned between dissolved and particulate phases.

Hg^0 is assumed only in its dissolved form while $\text{Hg}(\text{II})$ and MeHg are modelled as sorbing to sand, silts, and biotic solids and as being complex with dissolved organic carbon (DOC).

The model addresses the bioaccumulation of mercury in biota simply by dynamically modelling primary production and degradation processes of the 'organic solids' variable, which is subjected to production and dissolution. Production (eq. (1.2)) is parameterized based on a rate k_{pp} ($\text{g}/\text{m}^3 \text{ d}$) corrected by the temperature value ($\theta_{pp}^{T-20} \cdot X_t$) and it can be variable in space and time (using the X_{box} multiplier). In a similar way, degradation is parameterized based on a rate k_{deg} (1/d) that can be temperature-corrected and that is multiplied by the concentration of organic solids (C_{OM}) in that box:

$$\text{Production} = k_{pp} \cdot \theta_{pp}^{T-20} \cdot X_t \cdot X_{box} \left[\frac{\text{g } dw}{\text{m}^3 \text{ day}} \right] \quad (1.2)$$

$$\text{Degradation} = k_{deg} \cdot \theta_{deg}^{T-20} \cdot X_t \cdot X_{box} \cdot C_{OM} \left[\frac{\text{g } dw}{\text{m}^3 \text{ day}} \right] \quad (1.3)$$

The model dynamically simulates transformations (S_{rx} , eq. (1.1)) by means of first order rate constants. The modelled transformation processes are graphically presented in Fig. 2 and include the following: the photo-oxidation of Hg^0 into $\text{Hg}(\text{II})$ in water, the photo-reduction of $\text{Hg}(\text{II})$ into Hg^0 in water, the photo-degradation of MeHg into Hg^0 in water, the biotic methylation of $\text{Hg}(\text{II})$ into MeHg in water and sediments, the biotic demethylation of MeHg into $\text{Hg}(\text{II})$ in water and sediments.

Mercury: 1) is transported through water fluxes in dissolved and particulate forms; 2) is diffused in interface water/sediment in its dissolved form; 3) volatilises at the water/air interface; and 4) is

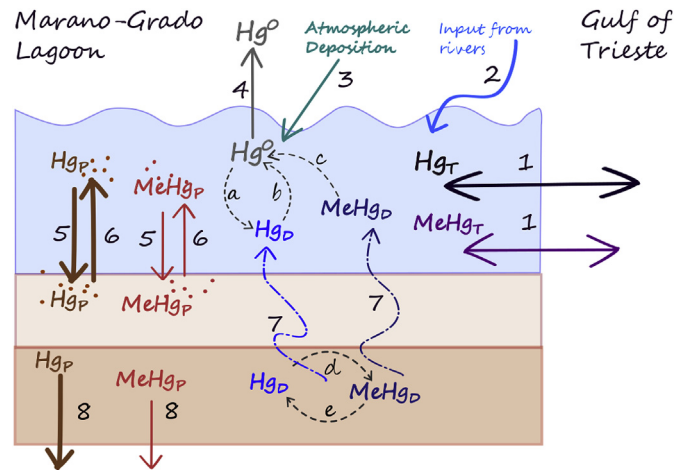


Fig. 2. Graphical representation of the mercury model. Hg_T is total Hg ($\text{Hg}^{\text{II}} + \text{Hg}^0 + \text{MeHg}$ in dissolved and particulate phase), MeHg_T is total MeHg (dissolved and particulate phase of MeHg), Hg_P and MeHg_P are particulate-bound Hg^{II} and MeHg, whilst Hg_D and MeHg_D are the dissolved forms of Hg^{II} and MeHg. Numbers 1–8 indicate transport processes (1-Exchange with the Sea, 2-Input from rivers, 3-Atmospheric deposition, 4-Volatilization, 5-Deposition, 6-Resuspension, 7-Pore water diffusion, 8-Burial) letters a-e indicate transformation processes (a-Photo-oxidation, b-Photo-reduction, c-Photo-demethylation, d-Methylation, e-Demethylation) (adapted from Melaku Canu et al., 2015).

sedimented or resuspended at the sediment/water interface in particulate form.

Hg^0 exchange between surface water boxes and the overlying atmosphere is dependent on water and air concentrations of elemental Hg (Hg_w^0 and Hg_{atm}^0 in mg/L) and temperatures following Henry's law. Hg species exchange at the sediment layer/water interface is controlled by deposition and resuspension rates of organic and inorganic solids and pore water diffusion.

Resuspension and the settling of mercury species bounded to organic and inorganic solids are simulated dynamically in time at the sediment/water interface as a function of flow velocity, shear stress, and particle size. As velocity decreases the shear stress along the underlying sediment decreases, thereby decreasing the suspension velocity and increasing the settling velocity.

The lagoon system is represented as an 18-box system that are divided into 6 sub-basins (Lignano, S. Andrea, Buso, Morgo, Grado and Primero) according to the hydraulic zonation configuration proposed by Dorigo (1965). Each sub-basin is represented in the model as including the following three layers: a water layer, a surface sediment layer (0–2 cm depth) and a subsurface sediment layer (3–10 cm depth). Sub-basins are interconnected as shown in Fig. 1b, and each is connected to the marine and overlying atmospheric boundaries. Three of them (Lignano, Buso and Grado) are connected to three additional water boxes representing their tributary rivers. Exchanges of water, suspended particulates and Hg species occur at each intersection between sub-basins and boundaries.

Water transport between the 6 lagoon water boxes and with marine boundaries is simulated using prescribed water fluxes. Water fluxes were computed on purpose using a validated finite element hydrodynamic model of the Marano-Grado Lagoon (Ferrarin et al., 2010) forced with a 3-year set-up (2009–2011) that includes the following: water levels at marine inlets, meteorological forcings (hourly solar irradiance, precipitation, wind speed and direction) and riverine discharge.

The dynamical evolution of mercury species is modelled as a function of meteo-climatic data and is included in the model as daily forcing functions of light intensity, daylight hours, and

monthly water temperature. The model can, therefore, reproduce the temporal variability of methylation-demethylation and photo-reactions (photo-demethylation, photo-reduction and photo-oxidation) while the partitioning of mercury species (Hg_T and MeHg) occurs at constant rates in time and space.

Transport coefficients and transformation rate constants were selected according to studies conducted in the Marano-Grado Lagoon (Covelli et al., 2008; by Hines et al., 2012) and other similar environments when local information was not available (Hammerschmidt and Fitzgerald, 2004; Monperrus et al., 2007; Rothenberg et al., 2008; Sorokin et al., 1996; Whalin et al., 2007; Vost et al., 2012; US EPA, 1988, US EPA, 2009).

Marine exchange with the Adriatic Sea was simulated through the advection of dissolved and particulate Hg (Hg_D and Hg_P) and MeHg (MeHg_D and MeHg_P) according to the prescribed water flux variable in time and space and according to monthly variable concentrations of particulate matter (SPM). This information was derived from our dataset (Horvat et al., 2003; Regione FVG, 2013) as explained in Melaku Canu et al., 2015).

River inputs are given as unidirectional inputs of water, as dissolved and particulate Hg and as MeHg. Hg is input at the atmospheric boundary via deposition using the seasonal values given by Žagar et al. (2007).

The model was set up in agreement with Melaku Canu et al. (2015) using the three-year scenario set-up for 2009–2011, the time frame for which a complete series of dissolved mercury concentrations in the lagoon water and meteorological data are available. The model was initialised using space variable field data of sediment compositions (silt, sand and OC) and mercury sediment concentrations (Hg_T , Hg_S and MeHg) according to Acquavita et al. (2012). Concentrations in the water column were set to 0. Additional information on the model's implementation; parameter selection methods; and comparisons between experimental data on Hg_D and deposition, erosion and burial rates are given by Melaku Canu et al. (2015). Despite the model's simple spatial discretization, data comparisons confirm the model's capacity to reproduce the selected processes. Average sediment deposition values, erosion values and burial rates computed from the model based on values of shear stress induced by currents are in agreement with experimental values measured by Bloom et al. (2004) and Covelli et al. (2012).

The baseline scenario, Reference simulation (Ref), was used here to assess the recovery time of surface sediment under the assumption that external conditions remain as they are now (i.e., recursively applying the three-year set-up of forcing and boundary conditions). At the marine boundary, the concentration of dissolved mercury (Hg_D) and of mercury bounded to suspended sediments (Hg_P) is mainly related to inputs delivered by the Isonzo River (Covelli et al., 2012; Rajar et al., 2000) and discharged into the Adriatic Sea in the Gulf of Trieste (see Fig. 1a). Even though Hg_T at the marine boundary is expected to decrease in the future, as a consequence of the mine's closure in 1996, according to Covelli et al., 2012 in the short term, such a decrease is unlikely to occur. Gosar (2008) noted that mercury concentrations in river sediments in the Idrjca and Isonzo-(Soca) Rivers have not decreased over the past 15 years since mining activities have stopped due to the extent of historical discharge still present along the rivers banks. Therefore, we applied a precautionary approach by maintaining existing Hg_T input values throughout the whole simulation. In addition, we explored uncertainties in changes in forcing and boundary conditions by applying the following three additional scenarios: a) the increase in water temperature according to climatic change (CC) scenarios, b) the sea level rise High water Level scenario (HwL) and c) the removal of mercury inputs from the riverine boundaries (NoR). All of these simulations were run for 100 years and then

compared.

The CC scenario was applied according to Lazzari et al. (2013), who modelled the effects of climate change on the biogeochemistry of the Mediterranean Sea following the IPCC's SRES A1B scenario conditions (Nakicenovic and Swart, 2000). For 2070–2100, they predicted a warming of Northern Adriatic Sea surface water of 2.5 °C both in the winter and summer. This temperature increase was, therefore, applied to the water temperature time series while all other forcings and parameters were the same as those used in the Ref simulation.

The HwL scenario was applied by introducing changes in water fluxes in agreement with the results of the hydrodynamic model simulation of a sea level rise scenario. The sea level rise scenario was simulated by increasing sea level values at marine boundaries of 0.315 m in agreement with Lambeck et al. (2011).

Moreover, the sediment recovery time was assessed through a long-term simulation by running the baseline Ref simulation until surface and subsurface sediment met the legislative limit of 0.3 ppm. This result was compared with results obtained from running a simulation that excluded mercury inputs from the Adriatic Sea while setting the sea Hg_T to 0 as an extreme case of mercury input reduction.

3. Results

After 100 years, the Ref simulation shows a general decrease in Hg_T concentrations along the Lagoon surface (Fig. 3) and subsurface sediments (Fig. 4). The average reduction in the two sediment layers of the whole lagoon is –63% with more pronounced decreasing trends found in the Primero (–86%) and Morgo (–93%) sub-basins.

After an initial increase at the start of the simulation, MeHg tends to decrease and stabilize with asymptotic behaviour, on average increasing at the end by 43% in surface sediment and by 1.2% in the water column as shown in Table 1. At the end of the simulation, concentrations decrease in S. Andrea and Primero by –20% and –64% in surface sediments, respectively, and increase in the Lignano, Buso Morgo and Grado sub-basins by 102%, 81%, 22%, and 139%, respectively.

MeHg concentrations tend to increase in subsurface sediment (Fig. 4, Table 1), reaching a pseudo-stable value in some sub-basins (S.Andrea, Primero and Morgo) and maintaining an increasing trend towards the end of the simulation for the others.

In response to high frequency signals (e.g., tidal exchanges and solar radiation), Hg_T concentrations in lagoon water (Fig. 5) show higher levels of intra-annual variability than sediment concentrations. With time evolution, an overall (statistically significant ($p < 0.05$, Wilcoxon rank sum test)) decrease of –13% is observed for all sub-basins with minimal decrease found in Primero (–8%) and maximum decrease found in Grado (–15%). Water MeHg increases overall at a statistically significant level ($p < 0.05$, Wilcoxon rank sum test) by 11% in all of the sub-basins.

A scenario analysis was carried out at the sub-basin scale by comparing the evolution of total mercury (Hg_T) and methylmercury (MeHg) concentrations in surface sediments (0–2 cm), subsurface sediments (3–10 cm) and the water column as shown in Figs. 3–5. The percentage of the variation in mercury (Hg) concentrations in each scenario with respect to Ref conditions was computed for each sub-basin and then averaged for the whole lagoon as shown in Table 2.

The NoR simulation scenario was explored to address the effect of mercury riverine inputs on the recovery of lagoon sediment. Computed concentrations of the NoR scenario at the end of the 100-year simulation were compared with the Ref, revealing a small decrease in Hg_T at the surface (Fig. 3) and subsurface sediment

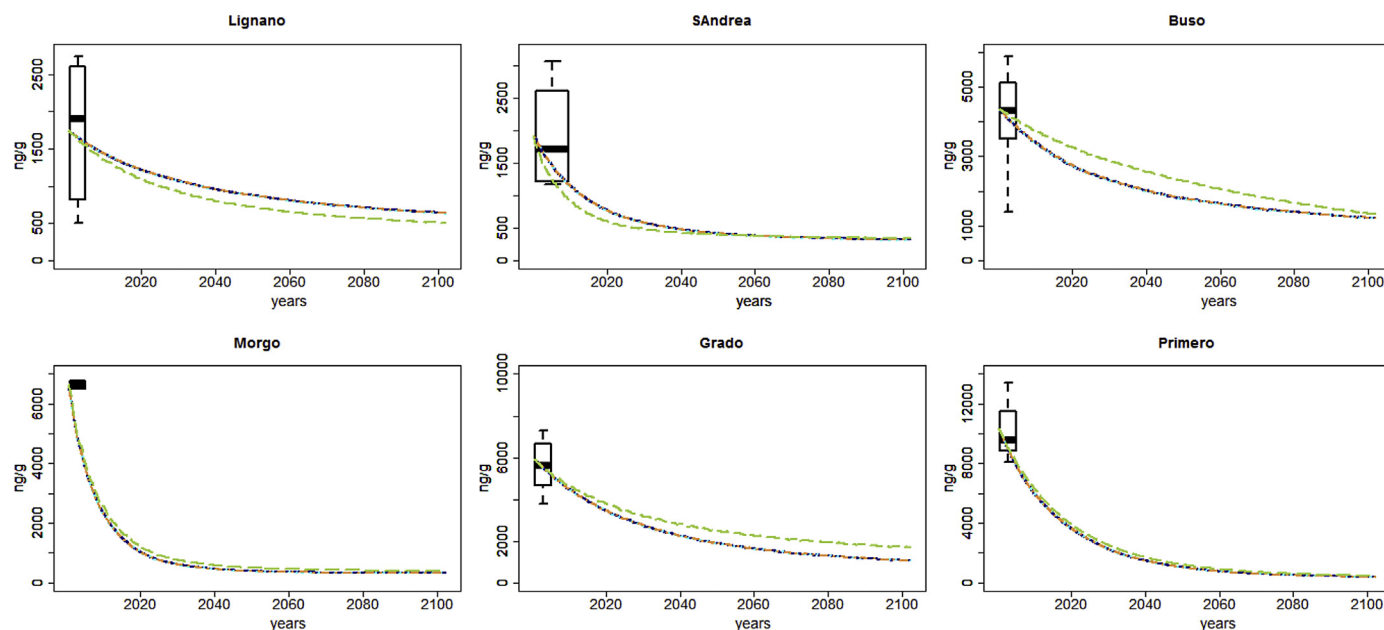
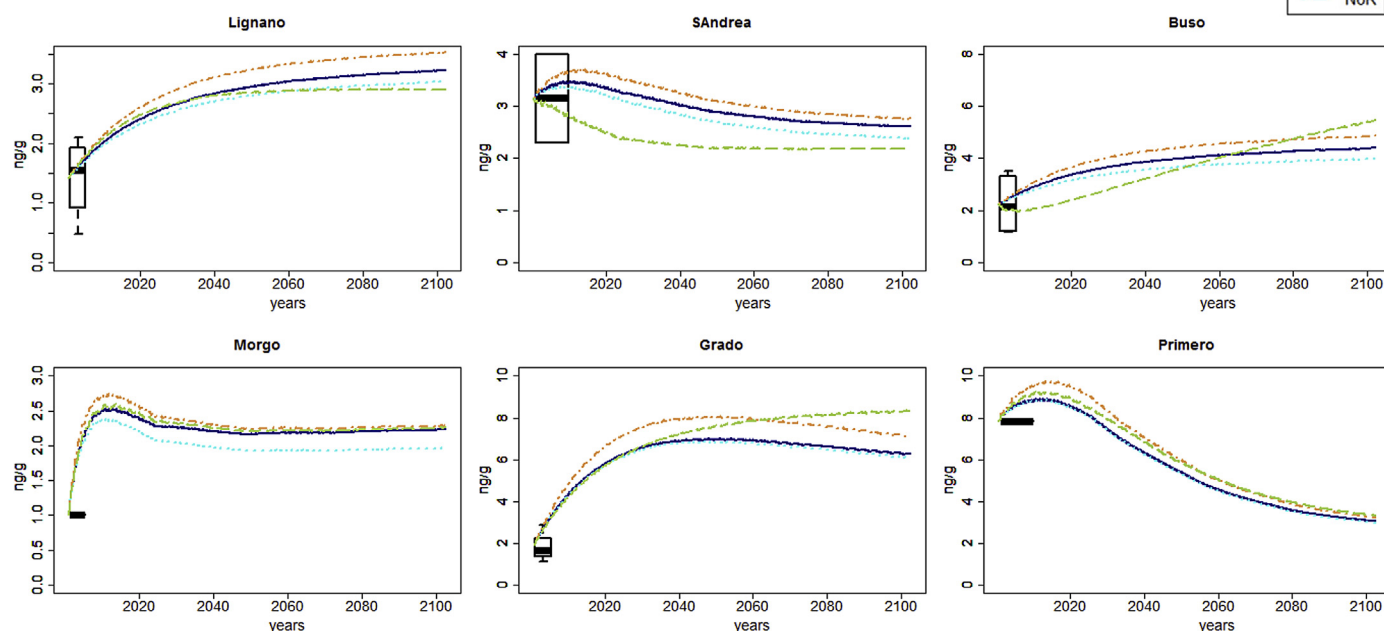
Hg_T concentrations in the surface sedimentMeHg_T concentrations in the surface sediment

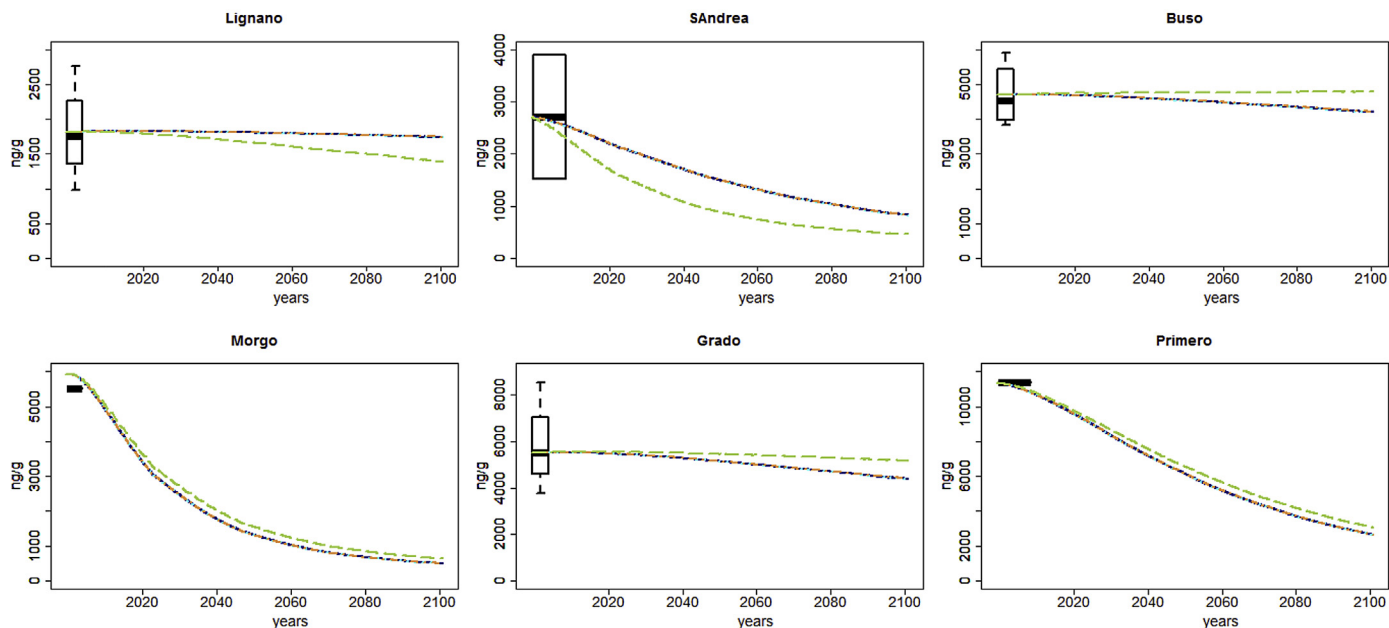
Fig. 3. Time evolution Hg_T (upper panel) and MeHg (lower panel) concentrations in surface sediment layers. Box plot: field data.

(Fig. 4) of 1.2% and 0.4%, respectively, and a decrease of Hg_T in water of 2.6% as shown in Fig. 5 and Table 2. Effects of the absence of riverine inputs on MeHg concentrations are more pronounced (Fig. 5), leading to a –12.5% reduction in the water column and decreases of 6.6% and 2.9% in the surface and subsurface sediment layers, respectively, as shown in Figs. 3 and 4 and Table 2.

Under the CC scenario, an average temperature increase of 2.5 °C over the whole simulation period has a negligible effect on Hg_T concentrations (as shown in Fig. 5 and Table 2) with respect to Ref while surface and subsurface sediments slightly increase or decrease depending on sub-basin conditions (as shown in Figs. 3

and 4). Methylation and demethylation processes, however, are more sensitive to temperature changes compared to the other transformation processes (Fig. 2); we, therefore, observed higher MeHg concentrations in the surface (8%) and subsurface sediments (13%) in the CC scenario with respect to the Ref. This effect could have been even more significant if the model had taken into account methylation processes occurring in the water column. Under the CC scenario, the transfer of MeHg from sediment to the water column is enhanced due to higher MeHg_D diffusion rates from pore-water (+12%) and higher due to MeHg_p resuspension rates (+11%). This affects the export of MeHg into the Adriatic Sea, which

Hg_T concentrations in the sub-surface sediment



MeHg_T concentrations in the sub-surface sediment

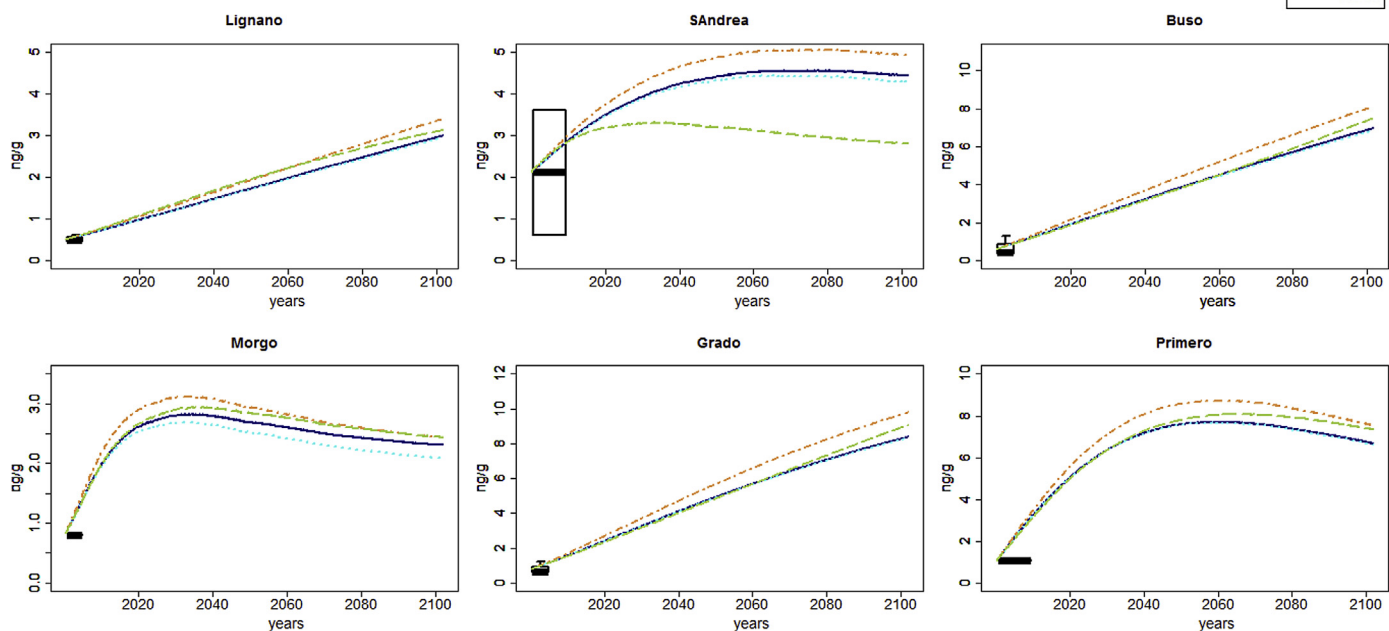


Fig. 4. Time evolution of Hg_T (upper panel) and MeHg (lower panel) concentrations in subsurface sediment layers. Box plot: field data.

increases by 2.7%. As a consequence, MeHg_p burial in deep sediments increases as well (+11%). Higher temperatures also affect exchanges between surface water and the atmosphere, causing a 1%

Table 1
Summary of the average percentage of variations (from the initial state) of Hg species concentrations in water, surface sediment and subsurface sediment by the end of the 100 years simulations scenario (Ref).

Compartment	Water		Surface Sediment		Subsurface Sediment	
	Depth	Average 1 m	0–2 cm	2–10 cm	Hg	MeHg
Mercury Species	Hg	MeHg	Hg	MeHg	Hg	MeHg
	-13%	+1.2%	-80%	+43%	-45%	+420%

increase in Hg (0) evasion. Hg_p and Hg_D budget processes are generally less affected than those involving MeHg.

Under the HwL scenario, water circulation in the lagoon intensifies, increasing velocities and consequently increasing Hg resuspension. As this effect is especially more pronounced in the eastern Primero, Grado and Morgo basins and almost negligible in the western part of the lagoon, contrasting changes in the eastern and western sub-basins are observed. As shown in Fig. 5 and Table 2, a general increase of Hg_T in water is observed in the whole lagoon with respect to Ref, varying from 15% in Morgo to 0.5% in Lignano. A general increase in Hg_T and MeHg is observed in sediment and subsurface sediment (up to 58% and 33% for Grado

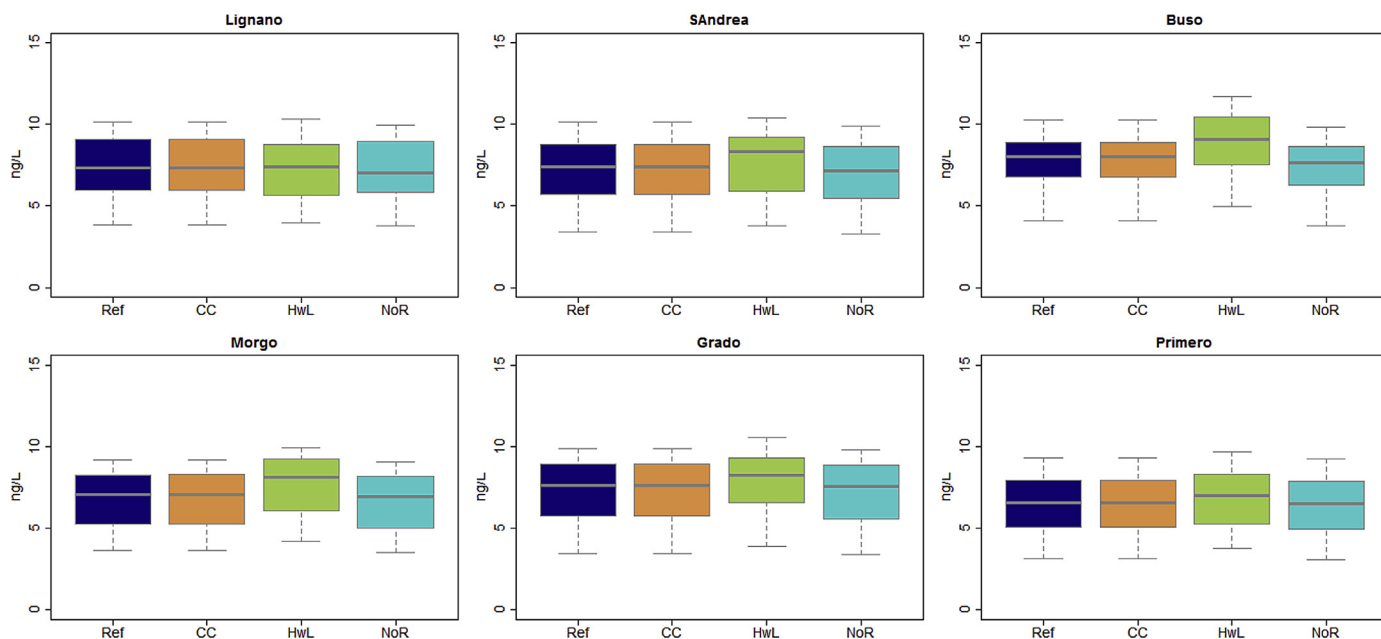
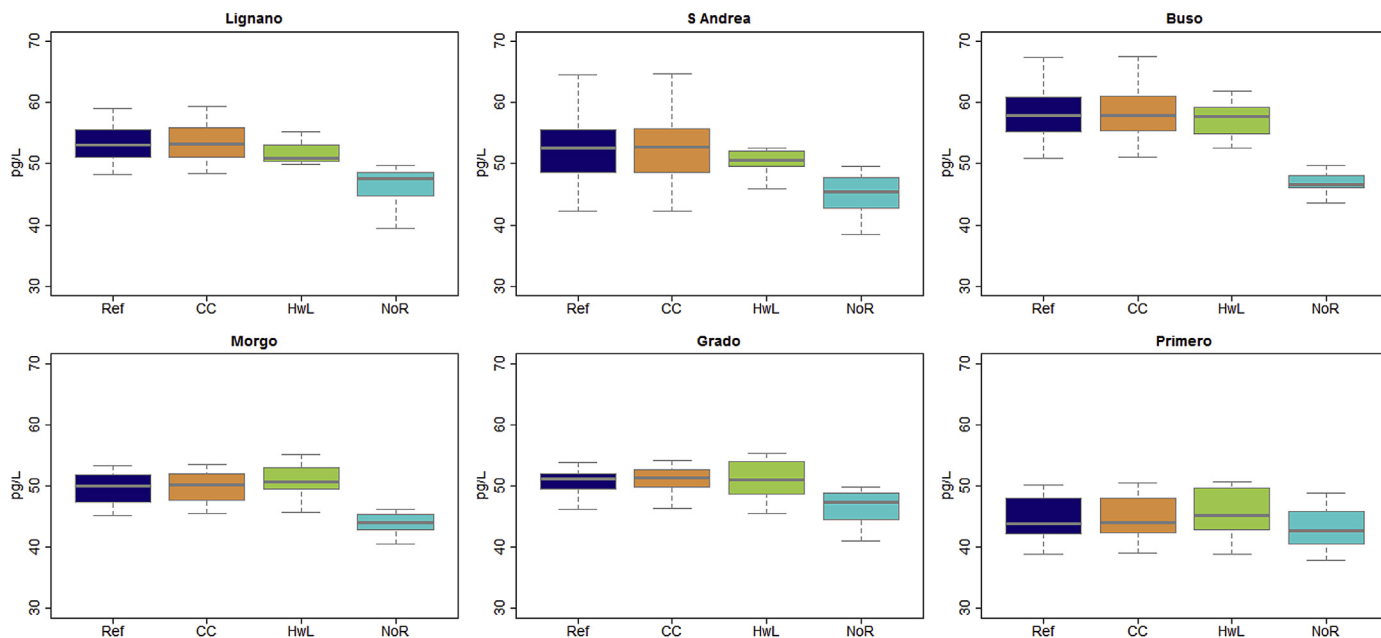
Hg_T concentrations in the lagoon watersMeHg_T concentrations in the lagoon water

Fig. 5. Box plots of concentration of Hg in the water column at the end of the scenario simulations: Hg_T (upper panel) and MeHg (lower panel). The graphs show the median; the 1st and 3rd quartiles; and minimum and maximum values for each simulation.

Table 2

Variations in Hg species concentrations in water, surface sediment and subsurface sediment by the end of the 100 years simulations scenario (NoR, CC, and HwL) relative to that of the Ref scenario by the end of the 100-year period. Values in brackets show the range of variation values computed for the six boxes when they have opposite signs.

Compartment Depth	Water		Surface Sediment		Subsurface Sediment	
	Average 1 m		0–2 cm		2–10 cm	
	Hg	MeHg	Hg	MeHg	Hg	MeHg
NoR	–2,6%	–12,5%	–1,2%	–6,6%	–0,4%	–2,9%
CC	<0,1%	0,4%	(±0,3%) 0,3%	8%	(±0,2%) 0,2%	13%
HwL	9%	(3%, –2,3%) –0,2%	(58%, –21%) 15,2%	(32%, –16%) 6,8%	(26%, –45%) 2%	(26%, –5%) –0,2%

surface sediment Hg_T and MeHg, respectively; 26% for Morgo subsurface sediment Hg_T ; and 10% for Primero MeHg). A decrease is observed in the western basins (up to -21% for Lignano surface sediment Hg_T , -45% for S. Andrea subsurface sediment Hg_T , and -16% and -37% for S. Andrea surface and subsurface sediment MeHg, respectively).

Overall, sediment concentrations in the water column are higher in the HwL than in the Ref simulation, promoting Hg and MeHg partitioning into sediment and decreasing Hg^0 evasion (-26% with respect to Ref). In the HwL scenario, the overall mercury budget is changed by a net increase of Hg_T outputs from the lagoon to the sea with respect to Ref.

The sediment recovery time was computed for the Ref simulation baseline scenario as the time required for surface sediment to reach the contamination level limit of Hg_T of 0.3 mg/kg set by Italian legislation under the EU–Water Framework Directive (Ministry of Environment Decree, 28/11/2010 n° 260, WFD, 2000/60 EU).

Under baseline conditions, the averaged recovery time for all lagoon surface sediments (weighted over the surface of each box) is 570 years, ranging from 50 years in Morgo to 1040 years in Buso depending on initial concentrations and on transport and transformation processes acting on each sub-basin. The sub-surface sediment averaged recovery time is much longer (1250 years) and ranges from 108 years in Morgo to 1750 years in Lignano and Buso. With the simulation run fully removing Hg inputs at marine boundaries (NoM), 0.3 ppm average concentrations in surface sediment are achieved 5 times faster relative to the Ref scenario, being reached after only 110 years.

Conversely, the removal of direct river mercury inputs from the simulation does not have a significant impact on average sediment recovery times.

4. Discussion

In this paper, we modelled the evolution of the mercury system in a hot spot of the Northern Adriatic Sea to project this system's evolution over the next 100 years while also considering climate change scenarios. The analysis was performed to contribute insight on relevant processes and on relative contributions of external boundaries and climatic conditions to overall budgets and dynamics. Hg budgets have been computed and compared for the scenarios, as reported in Fig. 6. In addition, a long term run was used to estimate the time required to reach sediment concentration values prescribed under environmental legislation. The model results highlight the relevance of the marine boundary to overall processes and, in particular, to mercury dynamics present in the water column, which are mainly driven by boundary conditions. However, the evolution of sediment concentrations is mainly driven by processes acting within the sediment and at the water/sediment interface. Such processes include sediment resuspension/deposition dynamics and methylation/demethylation processes, which in the model are, respectively governed in large part by water circulation dynamics and environmental conditions, and namely by temperature and solar radiation levels.

The model was applied in a 6-box configuration of the horizontal dimension. This configuration is more efficient than finer scale resolution models used, for instance, for the computation of water fluxes between boxes. It, thus, allows one to perform long-term scenario simulations. Another simplification commonly applied and accepted for model applications (Amos et al., 2014, 2015; Soerensen et al., 2010, 2016; Sunderland and Mason, 2007) pertains to the simple representation of Hg uptake by phytoplankton and its bioaccumulation in the trophic chain. Indeed, mechanisms of Hg uptake by phytoplankton are more complex in

Hg budget for each scenario [kg/y]

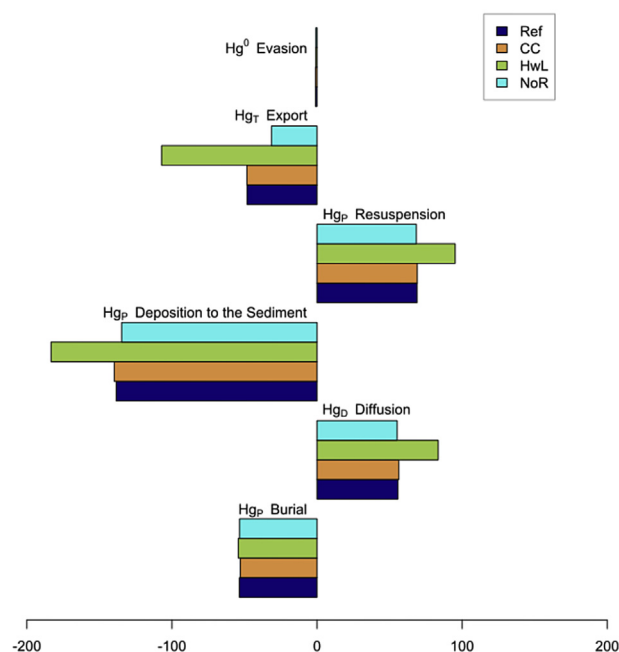


Fig. 6. Mass budget for Hg_T by the end of the 100 years simulations scenario (for the 4 scenarios: Ref, NoR, CC, and HwL).

reality (Le Faucheur et al., 2014). However, Sunderland et al. (2010) have shown that this process only contributes to a small portion of the overall budget in Passamaquoddy Bay. Despite its simplicity, the model allows one to identify major Hg lagoon dynamics and reproduce sediment deposition, erosion and burial processes. Comparisons drawn between monthly measures of dissolved mercury (Hg_D) in the water column and with particulate MeHg ($MeHg_p$) content in surface sediment have shown satisfactory agreement with field data (Melaku Canu et al., 2015). The model reproduced spatial variability between boxes and year-round temporal variability according to limits set by the model resolution, by the resolution (both in time and space) of field data, and by the time resolution of boundary conditions.

Results of the Ref simulation on long-term mercury budget trends in the Marano-Grado Lagoon show that sediment will continue to act as a secondary source of contamination in the long run. However, after 100 years of simulation conducted at the baseline, current Hg_T concentrations in the surface and subsurface sediment levels will decrease, inducing a net decrease (-57%) in Hg_T export to the sea over time that will change from 112 kg/y of the present state to 48 kg/y over 100 years with a net future MeHg export level of 0.63 kg/y . Hg_T concentrations in surface and subsurface sediment will slowly decrease overtime due to transport processes (e.g., burial in the deepest sediment and transferring to the water column followed by export to the Adriatic Sea or volatilization). The model predicts that surface sediment (the first 2 cm) will be recovered in all sub-basins after 1000 years, but it will be 500 years more before concentrations decline in subsurface sediment (3–10 cm in depth). Interestingly, the decreasing trend observed for Hg_T is decoupled from MeHg decontamination. After 100 years, the change in MeHg export will be almost negligible, with its formation and export related to environmental conditions and not limited by the predicted decrease in subsurface sediment Hg_T concentrations.

Recovery times were computed assuming that boundary

concentrations and global mercury dynamics do not change in the future. This is clearly an approximation based on the best data currently available and based on data and model collation. This estimate is not meant to be used as an official value but as information useful for determining the extent of historical mercury pollution based on a time-focused perspective.

However, an unbridgeable uncertainty regarding boundary and forcing condition values must be taken into account when considering such a long time frame, and such computations have only to be taken as broad indications of timescales of recovery and not as exact estimations of recovery time. Other set-ups could be developed if global mercury models (projecting overall changes in mercury circulation in a coupled ocean-atmospheric system based on future climatic and socio-economic scenarios) were available. Without such information, we prefer to use existing boundaries instead of drawing subjective assumptions on global trends while remembering that our scenario could be considered as precautionary because in the long run mercury inputs from the Isonzo River through the Adriatic Sea could decline considerably.

To apply a minimum (but unrealistic) limit to our computation of recovery time, a NoM simulation was run after removing Hg inputs at marine boundaries; this generated an average recovery time of only 110 years.

Conversely, the removal of direct river mercury inputs to the lagoon (NoR scenario) did not significantly change average sediment recovering times. The simulation allowed us to explore the effects of a hypothetical decontamination intervention on river basins (e.g., mercury capping) as an indication of the benefits of such an intervention for a given system. The model shows that riverine input removal has minimal effects on Hg_T mercury concentrations in surface and subsurface sediments and the water column. Effects on MeHg concentrations are instead more evident in sediments and the water column as shown in Fig. 5. An overall effect, however, is found at the end of the 100-year simulation, with a decrease in mercury exports to the Adriatic Sea for Ref (35% for Hg_T and 94% for MeHg) and with a reduction in Hg_T concentrations in surface sediment as described above (exports of Hg_T of 31 kg/y and only of 0.04 kg/y of MeHg).

For the CC scenario, we assessed the effects of temperature increases on mercury dynamics in the Marano-Grado Lagoon without making any other assumptions on changes in Hg_T concentrations at boundaries related to either temperature changes or socio-economic scenarios. The net MeHg sea export level is slightly higher (by 3%) while the Hg_T export level is almost the same. Higher temperatures fuel higher bacterial metabolic rates that enhance methylation (and demethylation) activities. However, methylation prevails over demethylation, resulting in higher MeHg concentrations in surface and sub-surface sediments with potential effects on the trophic chain. Conversely, Hg_T concentrations in sediments and water do not change significantly relative to Ref ones, being mainly driven by marine boundary values. The effects of increasing methylation and demethylation rates are much less significant in water column MeHg concentrations (+0.17%) due to the effects of intense water circulation and exchanges with seawater. However, we speculate that temperature increases can lead to longer periods of stratification in shallow lagoon water, a condition that is known to promote bottom anoxia, to enhance diffusion from pore-water (Emili et al., 2014) and favour optimal zone shifting for methylation from sediments to the water column (Fitzgerald et al., 2007). Moreover, increasing temperatures can induce an increase in MeHg levels in surrounding coastal systems, including at river mouths. Therefore, our set up may underestimate MeHg concentrations in the lagoon. In addition, our representation of sediment-water transport could be somewhat underestimated for all scenarios due to model limitations concerning the following: 1) the use of a

partition constant (K_D) fixed in time and space and 2) the use of Fick's law to calculate diffusion processes that often cause underestimations of *in-situ* fluxes measured within a benthic chamber (Benoit et al., 1999).

When removing boundary inputs, MeHg concentrations in water decrease dramatically (−79% in the NoM scenario, and −31% in the NoR scenario), and concentrations in surface and subsurface sediment decrease as well. This allows us to infer that riverine and marine inputs of Hg and MeHg play a key role in the accumulation of MeHg in sediment. In their absence, MeHg produced in sediment should be partly counterbalanced by demethylation and transport to the water column (followed by export, photo-degradation or deposition back to sediment). Marine boundary concentrations are clearly the main drivers shaping mercury dynamics in the Marano-Grado lagoon system and corresponding self-decontamination rates. As shown above, river inputs have a minor effect but are still important, and especially when considering net mercury fluxes between the lagoon and its boundary systems.

The sea level rise and increasing levels of water exchange at inlets tend to intensify all transfer processes directly related to water circulation. By the end of the 100-year run, the HwL shows (with respect to the Ref) an increase in Hg_T export towards the sea (+122%), diffusion (+48%), resuspension (+38%) and deposition (+32%). A minor change in burial rates is also observed. Despite negligible changes in water concentrations, MeHg and Hg_T levels in sediment increase by 7% and 15%, respectively, thus potentially increasing in biota as well. As both CC and HwL show an increase in MeHg concentrations in surface sediment, combined effects of sea level rise and temperature increases should reasonably lead to conditions of increased toxicity for local biota.

5. Conclusion

The Marano Grado lagoon is a large Mediterranean hot spot for mercury contamination. The lagoon has been receiving mercury discharge for centuries, and even if inputs from anthropogenic sources stopped decades ago, the lagoon's sediments still present high mercury concentrations and act as a secondary source for the whole Mediterranean basin. A scenario analysis performed based on a validated numerical model constrained by available data and information allowed us to assess short- and long-term dynamics of mercury contamination in this system. The model shows that based on the current configuration, 100 years from now, a decrease in Hg_T concentrations is expected in the system. Similarly, there should be an overall decrease in mercury flux within the lagoon system and between the lagoon and its surrounding boundaries. However, a general increase in MeHg is expected, and particularly in surface sediment (73%). Climate change should worsen this situation, causing increases in MeHg concentrations of up to 87% and 95% of current levels with respect to increasing temperatures (+2.5 °C) and sea level rise (0.315 m), respectively. Accordingly, mercury bioaccumulation in biota is expected to increase in the future.

Our simulation suggests that a complete removal of mercury inputs from rivers directly discharging into this lagoon would not substantially affect mercury dynamics besides reducing MeHg concentrations in water (12%) and surface sediments (6%). Interestingly, the reduction in MeHg as a consequence of the total removal of Hg inputs from rivers is of the same order as MeHg increase resulting from an increase in temperature or from sea level rise; therefore, the former may be envisaged as a possible way of mitigating adverse effects of the latter.

The long-term run of the baseline reference simulation indicates that recovery times of lagoon sediments computed as the time required to decrease Hg_T to 0.3 mg/kg are roughly 600 years for

surface sediments and 1200 years for sub-surface sediments. These lengths of time should be markedly shorter (110 years for sediment) for unrealistic scenarios involving no Hg inputs from the sea. Though unrealistic, such scenarios still offer a timescale for waste remediation measures needed for the system and serve as a framework for understanding this ecosystem service.

Acknowledgements

This research was carried out with contributions from the RITMARE flagship Project and with the contribution from the Friuli Venezia Giulia Regional Protection Agency (ARPA-FVG) in the frame of the EU-SHAPE project activities.

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