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PAPER

The key role played by the Augusta basin (southern Italy) in the mercury contamination of the Mediterranean Sea

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The Augusta basin, located in SE Sicily (southern Italy), is a semi-enclosed marine area, labelled as a highly contaminated site. The release of mercury into the harbour seawater and its dispersion to the blue water, make the Augusta basin a potential source of anthropogenic pollution for the Mediterranean Sea. A mass balance was implemented to calculate the HgT budget in the Augusta basin. Results suggest that an average of ~0.073 kmol of HgT is released, by diffusion, on a yearly basis, from sediments to the seawater, with a consequent output of 0.162 kmol y^{-1} to coastal and offshore waters; this makes the Augusta area an important contributor of mercury to the Mediterranean Sea. Owing to the geographical location of the Augusta basin, its outflowing shelf-waters are immediately intercepted by the surface Atlantic Ionian Stream (AIS) and mixed with the main gyres of the eastern Mediterranean Sea, thus representing a risk for the large-scale marine system.

1. Introduction

Mercury is considered a harmful element for land and marine ecosystems. Mercury also produces a wide range of adverse health effects in humans (*e.g.*, Clarkson,[1] Guzzi and La Porta[2]), mainly because of its ability to form organic complexes such as monomethyl mercury (MMHg) and dimethyl mercury (DMHg), and to bioaccumulate and biomagnify within food webs (Mason *et al.*,[3] Gill *et al.*,[4] Covelli *et al.*,[5] Langer *et al.*,[6] Hammerschmidt *et al.*[7]). The mercury biogeochemical cycle and accurate mass budgets have been constructed for the global ocean (Lamborg *et al.*,[8] Mason and Sheu,[9] Sunderland and Mason,[10] Outridge *et al.*,[11] Hare *et al.*[12]). Particularly, ocean waters seem to play a key role in modulating global mercury cycles (Mason *et al.*,[13] Mason and Sheu,[9] Laurier *et al.*,[14] Kotnik *et al.*[15]).

Natural and anthropogenic Hg (from mining industry, industrial plants, *etc.*) is introduced in the aquatic system by atmospheric deposition and direct river discharge. In turn, Hg (II), the main form of mercury in the atmosphere, can be reduced to elemental Hg(0) by aquatic microorganisms (Mason *et al.*[16]) or by photo-reduction (Amyot *et al.*,[17] Costa and Liss[18,19]). Most of the aquatic environments are supersaturated with respect to dissolved gaseous mercury (DGM) part of which is released into the atmosphere (Schroder and Munthe,[20] Mason *et al.*[13]). Recent data (*e.g.*, Mason and Sheu,[9] Cossa and Coquery[21]) have provided estimates of ocean mercury evasion that are three times larger (order of magnitude of 2600 t y^{-1}) than those measured for the atmospheric deposition.

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Environmental impact

The manuscript presents an unprecedented and high-quality dataset of HgT concentrations from the exceptionally contaminated sediments of the Augusta basin (southern Italy) and speculates about the key role played by this area in exporting mercury (HgT) to the Mediterranean Sea. Actually, the potential release of HgT from contaminated sediments outflowing the Augusta basin could definitively influence the HgT content of the Levantine Intermediate Waters with an effective large-scale contamination of the entire Mediterranean basin. Finally, the narrow continental margin off the Augusta coast, associated to steep slope and several gullies, creates preferential transfer routes for polluted sediments to the Mediterranean basin.

The fate of Hg in the marine system is affected by sorption/desorption processes onto suspended particulate matter and, based on associated kinetics, it may be partially transferred from surface waters to bottom sediments. Microorganisms, at the water/sediments interface such as sulfate reducing bacteria (SRB), mediate the transformation of inorganic Hg to MMHg with high rates of methylation favored by the presence of high content of organic matter (Lambertsson and Nilsson[22]) under reducing environmental conditions (*e.g.* Langer *et al.*[6]). Therefore, sediments are considered key contributors of MMHg to the marine ecosystem and recent estimates of emission from Mediterranean deep sediments are around $\sim$14 kmol y^{-1} (Ogrinc *et al.*[23]).

This study presents a mass-balance of total mercury (HgT) in the Augusta basin, an artificial marine area situated within the Augusta Bay, on the eastern coast of Sicily (Ionian Sea, southern Italy). The Augusta basin, which extends for about 23.5 km^2, covers part of the Augusta Bay, and is considered one of the most polluted areas of the Mediterranean Sea due to the careless discharge of Hg (since the 1950s) from industrial and petrochemical plants. In particular, the southernmost part of the Augusta basin hosted one of the most important chlor-alkali plants of Italy (Syndial Priolo Gargallo), which with 765 kg of Hg emission made up over 20% of total Italian emissions in 2001 (Le Donne and Ciafani[24]). The effects of this indiscriminate Hg discharge include the alarming high concentrations of the element recently measured in sediments of the basin (ICRAM,[25] Romano *et al.*[26]), prompting the Italian government to include the Augusta basin in the National Remediation Plan.

The large extension and high degree of contamination in the Augusta basin call for an appropriate investigation on the potential role played by this area in the impact of Hg contamination at Mediterranean scale.

Rajar *et al.*[27] calculated a total of 5400 kmol of HgT in the Mediterranean Sea and suggested that this basin is a net source of Hg to the atmosphere as well as to neighboring marine systems. The mass balance of Rajar *et al.*[27] takes into account the following primary Hg sources: atmospheric deposition (115 kmol y^{-1}), river influx (68.5 kmol y^{-1}), evasion from bottom sediments (80 kmol y^{-1}) and a total of Hg anthropogenic input estimated around 12.5 kmol y^{-1}. Main outputs of the mass-balance take into account the evasion of Hg to the atmosphere (249 kmol y^{-1}) and sedimentary burial (55 kmol y^{-1}). The net outflow through Gibraltar was measured to be 8.5 kmol y^{-1} and the net contribution from the Black Sea is limited to 0.3 kmol y^{-1}. The HgT mass balance proposed by Rajar *et al.*[27] did not consider the Augusta basin as a point source of HgT to the Mediterranean Sea. More recent studies have already documented high concentrations of HgT in Augusta offshore sediments, probably due to significant remobilization of sediments from the internal bay (Ogrinc *et al.*,[23] Di Leonardo *et al.*,[28,29] Romano *et al.*[26]) and described the potential risk for local marine ecosystems. On the other hand, no information is currently available on the potential risk associated with the impact of HgT released to the seawater from highly contaminated sediments to the seawater in the Augusta basin and associated dispersion at Mediterranean scale. For this reason, it appears essential to investigate the role of the Augusta basin as a critical point source of HgT for the Mediterranean Sea.

2. Materials and methods

2.1. Study area. The Augusta basin is within a natural bay, delimited in the northern sector by the Augusta town and closed to the South and East by artificial dams, which were built in the early '60s (Fig. 1). Two main inlets allow connection with the open sea: the Scirocco inlet, 300 m wide and 13 m deep, and the Levante inlet, 400 m wide and 40 m deep. The basin is characterised by three different circulation systems. Water circulation, in the Levante inlet, is dominated by a northward flowing affected by tidal forcing, with a mean velocity estimated to be around 18 and 7 cm s^{-1} at the surface and at the bottom, respectively. Similarly, the southern current at the Scirocco inlet flows parallel to the coast with moderate speeds (8 and 4 cm s^{-1} at the surface and the bottom, respectively). The northern portion of the basin, characterised by low seabed, is scarcely affected by active currents (ICRAM[30]). All the available data, concerning physico-chemical and hydrodynamical characteristics, were provided by the environmental characterisation carried out by the Deputy Commissioner for Waste Management Emergency and Water Conservation in Sicily and developed by ICRAM.[30] Recent "swath"-bathymetric surveys, carried out by IAMC-CNR (Budillon *et al.*[31]), evidenced the main features of the seabed between the Megarese harbour and the steep continental slope to the East (Fig. 1). A very narrow shelf develops down to 100–130 m with a mean gradient of about 1.0°. The shelf-border is quite sharp and approximately 4 km off the Levante gate; beyond it is the slope, which abruptly deepens by a mean value of about 15°, locally exceeding 25°. A dense net of gullies, often showing shelf-breaching heads, incise the seabed and merge towards the deep into V-shaped channels, thus forming a herringbone erosional pattern, typical of unstable slopes. The slope off the Augusta Bay is part of the Malta escarpment, a morpho-structural lineament, north–south oriented, of the Central Mediterranean Sea (Scandone *et al.*[32]).

2.2. Sampling and analyses

The results of this study concern the surface levels (0–10 cm) of 315 sediment cores collected in the year 2005. Sediment cores

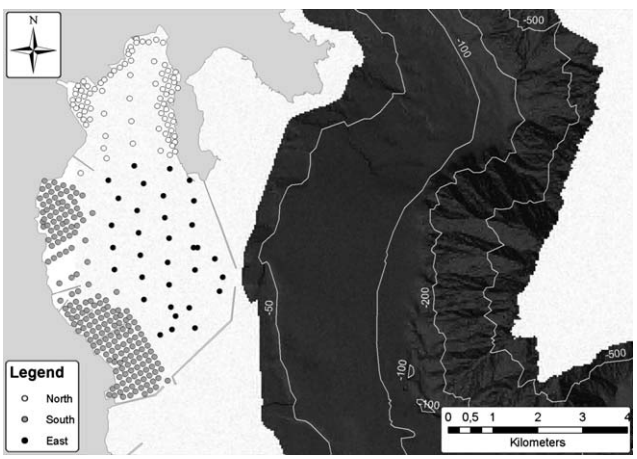

Fig. 1 Location map of the Augusta basin with sampling points referred to as the different contaminated areas of the basin (see text for details) and high-resolution swath-bathymetry of the external area.

were collected using a vibrocore and internal liner to preserve the sediment from potential and cross-over contamination. They were, successively, subsampled for the determination of physico-chemical analysis such as grain-size, metals and organic compounds (ICRAM[30]). In particular, mercury was determined using homogenised sample aliquots and analysed by Atomic Absorption Spectrometry (AAS), according to Giani *et al.*[33]

2.3. Geostatistical methods

In order to achieve the best estimate of HgT in surface sediments of the Augusta basin, statistical interpolation was performed by means of the block kriging technique (Fig. 3). In essence, kriging is a probabilistic interpolation method based on the theory of regionalized variables (Matheron[34]). Assuming that, for a given variable, the differences between values, observed at different locations, tend to be minimized as distances decrease, the degree of spatial continuity of the variable can be evaluated.

One of the most used indices of spatial continuity is the semi-variance measure defined as follows:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left(v_{xi} - v_{xi+h}\right)^2$$

where h is the so-called "lag distance", $N(h)$ is the number of pairs of sampling points separated by h, x is the sample position in the space, $v_{xi} - v_{xi+h}$ is the difference between the values of the i^{th} pair of sampling points separated from each other by h. The semi-variance is calculated for increasing (usually integer multiples) lag values so that plotting $\gamma(h)$ *versus* h values (experimental variogram) and fitting the points (variogram modeling) provide a model for spatial continuity. During interpolation, the value of each cell is calculated by using known neighbouring values (using a so-called "search radius"), and assigning to each of them a weight based on the calculated spatial continuity model.

In this work interpolation was performed using a grid with 100 × 100 m cells, and statistics derived from cross-validation was used to select the best neighbour search strategy. For each cell the total amount of HgT was calculated by taking into account the specific weight (SW) and volume of sediments according to the following equation:

$$\text{kg(Hg)}_S = [\text{Hg}] \times \text{SW} \times V$$

where [Hg] is the concentration of Hg (mg kg^{-1}), SW is the specific weight (kg l^{-1}), and V is the volume of sediments (l).

3. Results

Box–whisker plots in Fig. 2 show basic statistics of HgT distribution patterns in the northern, southern, and eastern areas of the Augusta basin (Fig. 2). Based on the different sources of contamination, the Augusta basin is subdivided into (i) a northern sector which extends from the peninsula of Magnisi to the Marcellino river and is mainly affected by municipal waste discharge of the town of Augusta, (ii) a south-western sector, close to the coast between the Marcellino river and the dams, where the most important chemical and petrochemical plants operate (Syndial Priolo Gargallo, ESSO, ERG, *etc.*), and (iii) an eastern sector which extends from the central area to the Scirocco gate and is directly influenced by industrial activities on the southern coast of the basin. Sediments in the southern part of the Augusta basin show the highest HgT levels (0.1–527.3 mg kg^{-1}) with a large range of variability (median value 23.8 mg kg^{-1}) while the northern area is characterized by sediments with HgT concentrations varying from 0.1 to 12.7 mg kg^{-1} (median value 1.1 mg kg^{-1}). Sediments of the eastern area exhibit values of HgT concentrations ranging from 0.1 to 17.3 mg kg^{-1} (median value 4.6 mg kg^{-1}). In the northern part of the Augusta basin, Inverse Distance Weighted (IDW) interpolation of HgT data shows Hg concentrations in the range of 0.2–47.8 mg kg^{-1}, and a limited number of hot-spots. The southern part of the Augusta basin (from the Pontile Cementeria down to the dam) is characterized by higher HgT concentrations with decreasing values from the coastline. The coastal area between the Pontile Superpetroliere and the Pontile Liquidi is the most HgT contaminated sector of the basin (Fig. 3A). The specific weight of sediments ranges from 1.2 to 1.7 kg l^{-1} (Fig. 3B). On the whole, higher SW values were measured in the southern and northern sectors of the studied area. It is noteworthy that in the south of the area, between the Pontile Cementeria and the Pontile Superpetroliere, an anomalous relatively lower specific weight zone occurs with values ranging between 1.2 and 1.4 kg l^{-1}.

4. Mass balance of HgT in the Augusta basin

A first-order box model that calculates the budget of HgT in seawater and sediments of the Augusta area is here tentatively proposed. The Augusta marine area can be basically considered as an "environmental compartment" with well-defined borders and constrained hydrodynamics. The seawater outflows at the bottom of the Levante and Scirocco inlets are about 7 and 6 cm s^{-1}, respectively (ICRAM[30]); this corresponds to an average output of water mass of ~2.34 × 10^{13} kg y^{-1}.

The mass balance of HgT in the basin is calculated at the steady-state by the following equation:

$$I + A + \text{AD} + R = O + D + V \quad (1)$$

where I represents the total Hg influx from the surface Mediterranean seawater, A represents the inputs of dissolved Hg from anthropogenic activities, AD corresponds to the atmospheric Hg deposition, R is the Hg re-suspension/release from sediments. On the other side, O is the total Hg outflow from the basin, D corresponds to sedimentary deposition and burial, and V is a term accounting for evasion of HgT to the atmosphere (Fig. 4). All the budgets and parameters described below are summarised in Table 1.

For Mediterranean seawaters Kotnik *et al.*[15] reported HgT concentrations of 1.46 ± 0.62 and 1.21 ± 0.32 pM in summer and spring, respectively. Such values correspond to an average input of Hg in the Augusta basin (I) of about 8.48 × 10^{-7} kmol y^{-1} from the Ionian Sea.

Values of anthropogenic HgT inputs to the basin (A), including discharge from wastewater treatment facilities and industrial activities, are reported in the European pollutant emission register (http://www.eper.sinanet.apat.it/site/it IT/Registro_INES/Ricerca_per_complesso_industriale/ricercaINES.html),[35] which shows a total of 0.018 t in water for the year 2005.

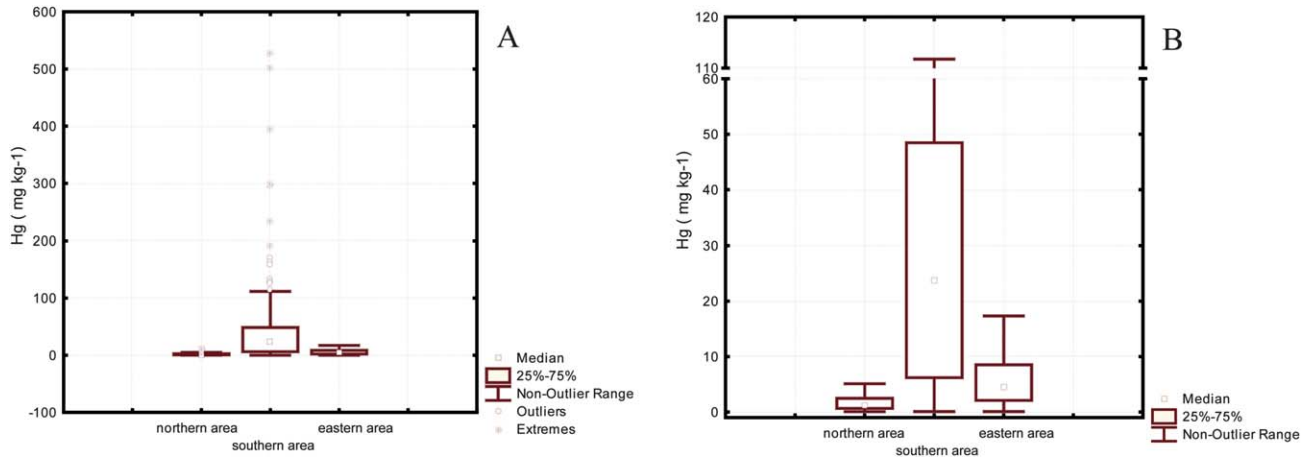

Fig. 2 Box–Whisker plots of HgT concentration in the sediments of the Augusta basin for the three different sectors (see text for details) characterised by different levels of contamination. (A) The range of HgT concentrations without outlier values (B) the range of HgT concentrations with outlier values.

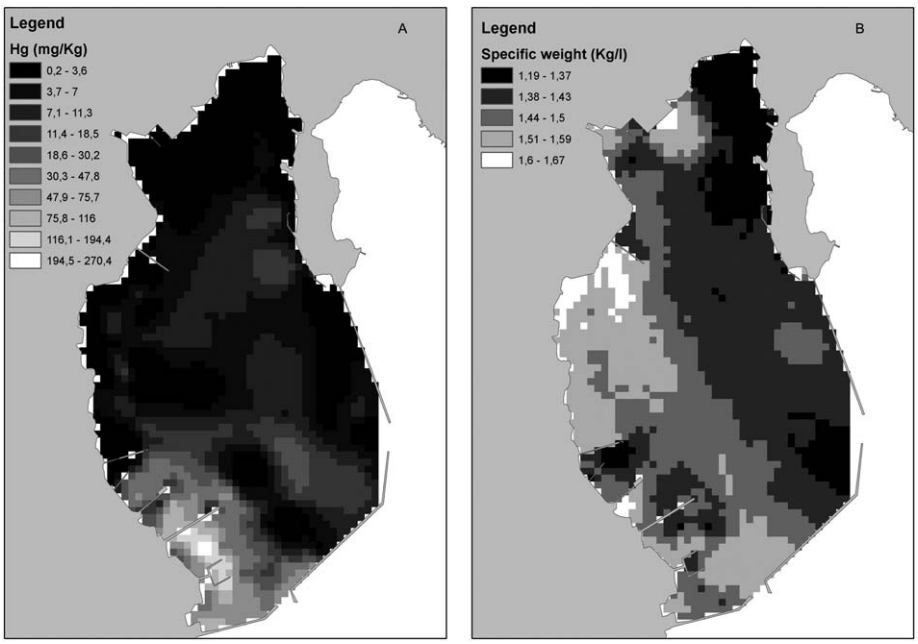

Fig. 3 Maps of interpolated values of (A) HgT concentrations and (B) specific weight. During interpolation task coastline was used as interpolation mask in order to take into account the effect of barriers.

Monthly, mean HgT depositions (wet + dry) calculated for the Mediterranean region by Strode *et al.*[36] were 1000 and 2500 ng m^{-2} in winter and summer, respectively. Accordingly, HgT AD for the Augusta area corresponds to an average of 2.44×10^{-3} kmol y^{-1}. On the other hand, the average HgT evasion (V) calculated for the entire Mediterranean Sea surface was an average of 383.86 kmol per year (Andersson *et al.*[37]), which corresponds to an average of 3.84×10^{-3} kmol y^{-1} for the Augusta basin. Since 2005, industrial activities of the chlor-alkali plant have been definitively dismissed and therefore D parameter can be considered null in our mass balance.

Flux of HgT from sediments to the water column (R) by pore-water diffusion and/or desorption from re-suspended contaminated particles is a key aspect in the Augusta basin due to the high levels of contamination measured in the area. Actually, mobility and availability of HgT depend on the nature and concentration of the binding phases in the sediment and on redox conditions of sediments. Usually, Hg is absorbed and co-precipitates with sulfide minerals (Gobeil and Cossa,[38] Gagnon *et al.*,[39] Wang *et al.*[40]) and can potentially be released into pore-water and eventually to overlying water *via* diffusion. Mercury can also be released as a result of microbial degradation of organic matter and chemical dissolution of sulfides due to redox variations during diagenesis pathways. Numerous studies document that Hg species and relative mobility increase in the overlying water with time, especially under conditions of relative "anoxia" (*e.g.*, Gill *et al.*,[4] Rajar *et al.*;[41] Tomiyasu *et al.*[42]). Particularly, Tomiyasu *et al.*[42] reported that about 33% of HgT

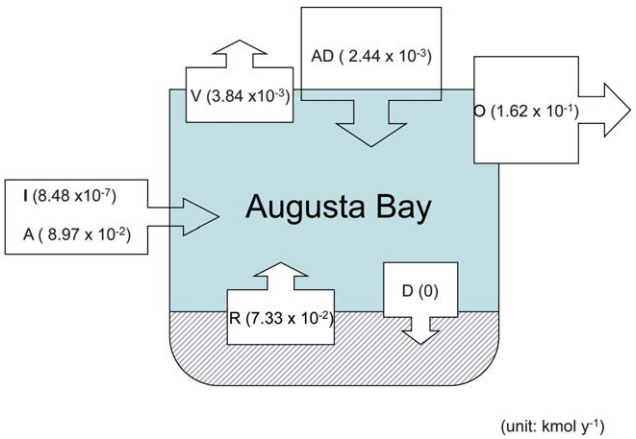

Fig. 4 Conceptual scheme for mass-balance calculation of HgT in the Augusta basin.

in sediment was released into the water column through re-suspension of particles in anaerobic systems, while a slightly greater percentage was found by Rajar *et al.*[41] for Hg re-suspension in the Hg mass balance established for the Gulf of Trieste.

The measured low Eh values and the high concentration of organic matter in the Augusta sediments (ICRAM[25]) have high potential for Hg release at the water/sediment interface and for significant diffusion from sediments to the water column. Presently, no measured benthic Hg fluxes are available for the Augusta basin sediments. Thus, in order to obtain a reasonable view of benthic fluxes from the sediments to the water column, the authors applied the values calculated and measured by Covelli *et al.*[5] in sediments highly polluted by Hg in the Gulf of Trieste. Considering the low Eh values measured in the Augusta sediments (median values of ~ -300 mV), the state of semi-closed environment of the basin and the low energy hydrodynamics of the system, it is reasonable to consider the disoxic/anoxic conditions of bottom sediments as being permanent. Hence, we contemplated the whole range of variability of benthic effluxes of Hg (27–6456 ng m^{-2} day^{-1} with an average of 1719 ng m^{-2} day^{-1}) measured by Covelli *et al.*[5] This value is one- to four-fold lower than those estimated in the Grado Lagoon (up to 33 200 ng m^{-2} day^{-1} Covelli *et al.*[43]) and in the San Francisco Bay-Delta (Choe *et al.*[44]), while the highest value is of the same order of magnitude of those reported by Bothner *et al.*[45] for marine sediments with high Hg pollution but different Eh and grain-size conditions. Information reported by ENVIRON[46] about the HgT concentration in pore-water of surface sediments of the southern and most contaminated area of the Augusta basin corresponding to a south-western sector in this study, range from 21.6 to 2550 ng l^{-1}. These are higher values than those reported by Covelli *et al.*[5] for samples where benthic fluxes were calculated. Thus, the application of benthic fluxes reported by Covelli *et al.*[5] to the Augusta system was considered conclusively reasonable and provided the best estimated benthic flux value. This implies that our assumption for HgT benthic flux from the Augusta sediments can reasonably represent the lower limit of the potential range measured in analogous marine environments. We are aware that only further and specific investigation on the actual HgT release from bottom sediments can improve this first order estimation. For the purpose of this paper, the active sediment layer, defined as the active bioturbation depth, directly involved in the exchange of HgT between the overlying water and sediments, is considered to be 0.1 m (Di Toro[47] and Di Toro and Fitzpatrick[48]). This layer can also be remixed by ship movements inside the bay, with a probable enhanced re-suspension/release of HgT from bed sediments. Considering an average value of benthic flux of 1719 ng m^{-2} day^{-1}, a total of 0.073 kmol (0.001 to 0.276 kmol y^{-1} considering the whole range of benthic fluxes reported by Covelli *et al.*[5]) is transferred yearly to the bottom water of the Augusta Bay. The residence time calculated for the bottom water of the Augusta, on the basis of the available hydrodynamic data, is about 10 months and therefore it is reasonable to assume that all the HgT released from sediments to the bottom seawater of the basin is flushed on a yearly basis and outflows to the eastern coast of Sicily. The calculated output of HgT from the Augusta basin to Ionian surface waters (O) corresponds to an average of $\sim$0.162 kmol y^{-1}. These first-order results (with an estimated average concentration of HgT dissolved of 0.075 nmol l^{-1}) seem to be in excellent agreement with the nine measurements of HgT in seawater reported for bottom, mid and surface waters by ENVIRON[46] with an average concentration of 0.25 nmol l^{-1} and a range of 0.05–0.37 nmol l^{-1}.

If specific research has to be planned to definitively constrain benthic fluxes of HgT from bottom sediments of the Augusta Bay, we are also convinced that other key parameters of eqn (1) require further investigation. In particular, inputs of HgT from land (parameter D in the equation) could be different from zero, as reported in the mass-balance, since even after the stop of the activity of the chlor-alkali plants using mercury technology, the channels of wastewater discharge could contain still Hg and could be supplementary inputs to the bay. Also, periods of intense flooding could provide remobilization of mercury in those channels and transport to the bay. This could limit the final budget to an estimation by defect with respect to a more realistic value. On the other hand, the term V (evasion HgT through the water–atmosphere interface) in eqn (1) represents a first-order approximation. Actually, the evasion of HgT to the atmosphere depends on several parameters including wind speed and dissolved gaseous mercury concentration that could be different in

Table 1 Parameters (sources and sinks) of HgT used to calculate the mass-balance of HgT in the Augusta basin

	I^a	A^b	AD^c	V^d	R^e	D	O
Units: t y^{-1}	1.70×10^{-7}	1.80×10^{-2}	4.90×10^{-4}	7.70×10^{-4}	1.47×10^{-2}	—	3.20×10^{-2}
Units: kmol y^{-1}	8.48×10^{-7}	8.97×10^{-2}	2.44×10^{-3}	3.84×10^{-3}	7.30×10^{-2}	—	1.62×10^{-1}

[a] Kotnik *et al.* (2007). [b] From the EPER database. [c] Strode *et al.* (2007). [d] Andersson *et al.* (2007). [e] Covelli *et al.* (1999).

such a highly contaminated area compared to the Mediterranean Sea. However, the impact of this parameter, on the final mass-balance of HgT in the bay, is limited (two orders of magnitude lower than the final estimated output from the bay) and we speculate that detailed information on that could not significantly change the achieved results.

Rajar *et al.*[27] reported a total input of Hg from anthropogenic sources to the Mediterranean Sea of ~12.5 kmol y^{-1} with a significant contribution from the Egyptian coastal area (6.8 kmol y^{-1}) but provided no information on the Augusta basin. The mass-balance here reported for the Augusta basin with an outflow value of ~0.162 kmol y^{-1} documents a potential role of this area as an important anthropogenic source of Hg contamination to the Mediterranean Sea.

5. Discussion

In view of the achieved results, the HgT mass balance for the Mediterranean Sea proposed by Rajar *et al.*[27] needs to be significantly revised in order to incorporate the Augusta as an important HgT point source to the basin. Indeed, the HgT input from the Augusta basin (0.162 kmol y^{-1}) appears to be a source of HgT for the Mediterranean Sea, increasing the value of 12.5 kmol y^{-1} estimated by Rajar *et al.*[27] Actually, by adding the estimated output of Hg input from the Augusta basin to the total mercury amount estimated by Rajar *et al.*[27] for the Mediterranean, the total HgT rises to 318.0 kmol y^{-1} (Fig. 5) with a resulting net outflow to the Atlantic ocean that varies between 40.9 and 40.7 kmol y^{-1}.

If *per se* the HgT budget of the outflow from the Augusta basin represents a primary concern as significant point source for the Mediterranean Sea, the effects of meso-scale circulation of the Ionian Sea create a higher potential risk for HgT contamination of the basin. Indeed, the Ionian Sea stands in the Eastern Mediterranean as the region mostly affected by the transit and transformation of the major water masses, which regulate the general thermohaline circulation in the upper, intermediate and deep layers, respectively (Malanotte-Rizzoli *et al.*[49]). In particular, the Atlantic Ionian Stream (AIS) flowing over the continental shelf off the southern Sicilian coast, in proximity of Cape Passero as an anticyclonic circulation, deviates over the Ionian slope northward to the Messina Strait flowing close to the

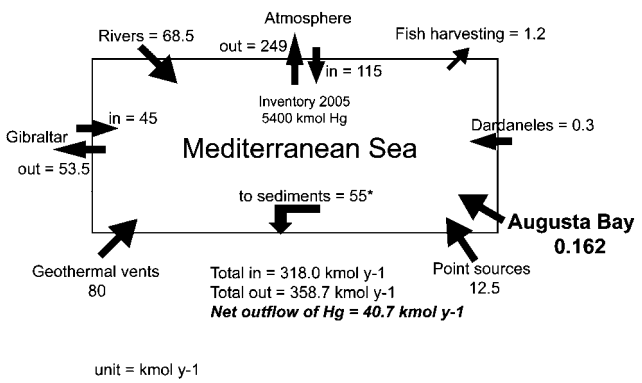

Fig. 5 HgT flows calculated for the Mediterranean Sea with the Augusta source point (modified by Rajar *et al.*[27]).

Augusta shelf (Lermusiaux and Robinson;[50] Napolitano *et al.*[51]). On the Augusta shelf, the coastal waters, at 30–60 m, mix with the Messina Mixed Waters (MMW) originating in the Strait of Messina and flow southward along the eastern Sicilian coast (Raffa and Hopkins[52]). The MMW extend for about 6.5 km offshore, and therefore a portion of this water is transported down to the Ionian shelf break where it mixes with AIS flow. Over the Ionian shelf break, in the summer, water circulation is controlled by predominant sub-basin-scale anticyclonic gyres that make this zone highly dynamic. In this scenario, the outflowing bottom waters from the Augusta basin have the high potential to contaminate an important portion of the surface water masses of the central-eastern Mediterranean by meso-scale ocean circulation. Interestingly, Kotnik *et al.*[15] measured the highest HgT concentrations of the Mediterranean Sea specifically in the Ionian seawaters during the spring of 2004.

Another critical point, in terms of potential risk associated to the transfer of Hg from the Augusta basin to the Mediterranean concerns the peculiar morphology of the continental margin off the Augusta coast, which is characterised by a narrow shelf and steep slope, with several gullies, dropping to the deep end of the Ionian basin (Fig. 1). This creates preferential transferring of polluted sediments from the internal Augusta basin, but also from the external part where past and uncontrolled dredging activities deposited part of contaminated sediments to the slope system and, consequently, to the Levantine Intermediate Waters (LIW). The LIW, flowing east to west in the Mediterranean, could represent an effective mechanism of large-scale spreading of HgT from the Augusta basin to the entire Mediterranean with unpredictable contamination effects on the entire basin.

6. Conclusion

This study has shown that the high levels of Hg concentration in the sediments of the Augusta basin, due to uncontrolled discharge of industrial plants, can be a primary source of Hg in the Augusta marine system. Taking into account the available data, the calculated mass of HgT present in the surface sediments (0–10 cm) of the Augusta basin was ~42 t, and the mass balance evaluation of HgT revealed that the outflow of HgT from the bay to the Augusta coastal waters was on average ~0.162 kmol y^{-1} (~0.032 t y^{-1}). Considering that these values correspond to ~1 to 2% of the amount calculated for the entire Mediterranean area (12.5 kmol y^{-1}), the Augusta basin plays an important role in exporting HgT into the Mediterranean Sea and represents a point source for that system. When the Augusta basin is considered as a point source of Hg in the mass balance proposed for Mediterranean Sea (Rajar *et al.*[25]), the net outflow of HgT from the Mediterranean Sea to Atlantic waters is 40.7 kmol y^{-1}. However, the most critical point related to the role played by the Augusta Bay in the Hg contamination of the Mediterranean Sea is associated to the outflow of bottom waters that intercept surface meso-scale ocean circulation with potential widespread contaminant distribution effects at basin scale. Finally, a narrow continental margin off the Augusta coast, associated to steep slope and several gullies, creates preferential transfer routes for polluted sediments from the internal Augusta basin, and also from the external part where past and uncontrolled dredging activities have deposited part of contaminated sediments on the

slope system. The potential release of HgT from contaminated sediments in that context could certainly influence the HgT content of the Levantine Intermediate Waters with an effective mechanism of large-scale contamination of the entire Mediterranean with unpredictable effects on the basin.

We are aware that the calculated HgT mass-balance for the Augusta basin follows only a first-order quantitative approach that needs to be supported by more definitive experimental data, currently unavailable for the studied environment. However, we also consider the presented results as a reasonable and reliable speculation on a new and complete dataset of an intensively polluted Mediterranean area valuable for planning further researches. Actually, despite the semi-quantitative values of HgT output from the Augusta basin we consider that the fundamental outcomes of our mass-balance clearly and vigorously demonstrate an essential role played by this area as mercury point-source for the whole Mediterranean Sea.

References

1 T. Clarkson, The toxicology of mercury, *Crit. Rev. Clin. Lab. Sci.*, 1997, **34**(4), 369–403.
2 G. Guzzi and C. A. La Porta, Molecular mechanisms triggered by mercury, *Toxicology*, 2008, **244**, 1–12.
3 R. P. Mason, N. M. Lawson, A. L. Lawrence, J. J. Leaner, J. G. Lee and G.-R. Sheu, Mercury in the Chesapeake Bay, *Mar. Chem.*, 1999, **65**, 77–96.
4 G. A. Gill, N. S. Bloom, S. Cappellino, C. Driscoll, S. Dobbs, L. McShea, R. P. Mason and J. Rudd, Sediment–water fluxes of mercury in Lavaca Bay, Texas, *Environ. Sci. Technol.*, 1999, **33**, 663–669.
5 S. Covelli, J. Faganeli, M. Horvat and A. Brambati, Pore water distribution and benthic fluxes measurement of mercury and methylmercury in the Gulf of Trieste (northern Adriatic Sea), *Estuarine, Coastal Shelf Sci.*, 1999, **48**(4), 415–428.
6 C. Langer, W. Fitzgerald, P. Visscher and G. Vandal, Biogeochemical cycling of methylmercury at Barn Island Salt Marsh, Stonington, CT, USA, *Wetlands Ecol. Manage.*, 2001, **9**, 295–310.
7 C. R. Hammerschmidt, W. F. Fitzgerald, C. H. Lamborg, P. H. Balcom and P. T. Visscher, Biogeochemistry of methylmercury in sediments of Long Island Sound, *Mar. Chem.*, 2004, **90**, 31–52.
8 C. H. Lamborg, W. F. Fitzgerald, J. O'Donnell and T. Torgerson, A non-steady state compartmental model of global-scale mercury biogeochemistry with interhemispheric gradients, *Geochim. Cosmochim. Acta*, 2002, **66**, 1105–1118.
9 R. P. Mason and G. R. Sheu, Role of the ocean in the global mercury cycle, *Global Biogeochem. Cycles*, 2002, **16**, 1093, 14p.
10 E. M. Sunderland and R. P. Mason, Human impacts on open ocean mercury concentrations, *Global Biogeochem. Cycles*, 2007, **21**, GB4022, 15p.
11 P. M. Outridge, R. W. Macdonald, F. Wang, G. A. Stern and A. P. Dastoor, A mass balance inventory of mercury in the Arctic Ocean, *Environ. Chem.*, 2008, **5**, 89–111.
12 A. Hare, G. A. Stern, R. W. Macdonald, Z. Z. Kuzyk and F. Wang, Contemporary and preindustrial mass budgets of mercury in the Hudson Bay Marine System: the role of sediment recycling, *Sci. Total Environ.*, 2008, **406**, 190–204.
13 R. P. Mason, W. F. Fitzgerald and F. M. M. Morel, The biogeochemical cycling of elemental mercury: anthropogenic influences, *Geochim. Cosmochim. Acta*, 1994, **58**, 3191–3198.
14 F. J. G. Laurier, R. P. Mason, L. M. Whalin and S. Kato, Reactive gaseous mercury formation in the North Pacific Ocean's marine boundary layer: a potential role of halogen chemistry, *J. Geophys. Res.*, 2003, **108**(D17), DOI: 10.1029/2003JD003625.
15 J. Kotnik, V. Fajon, D. Gibičar, L. Logar, N. Horvat, N. Ogrinc, M. Horvat, D. Amouroux, M. Monperrus, F. Sprovieri and N. Pirrone, Mercury speciation in surface and deep waters of the Mediterranean and Adriatic seas, *Mar. Chem.*, 2007, **107**, 13–30.
16 R. P. Mason, F. M. M. Morel and H. F. Hemond, The role of microorganisms in elemental mercury formation in natural waters, *Water, Air, Soil Pollut.*, 1995, **80**, 775–787.
17 M. Amyot, G. Mierle, D. Lean and D. J. Mc Queen, Effect of solar radiation on the formation of dissolved gaseous mercury in temperate lakes, *Geochim. Cosmochim. Acta*, 1997, **61**(5), 975–987.
18 M. Costa and P. Liss, Photoreduction of mercury in sea water and its possible implications for Hg0 air–sea fluxes, *Mar. Chem.*, 1999, **68**, 87–95.
19 M. Costa and P. Liss, Photoreduction and evaluationof mercury from sea water, *Sci. Total Environ.*, 2000, **261**, 125–135.
20 W. Schroeder and J. Munthe, Atmospheric mercury—an overview, *Atmos. Environ.*, 1998, **32**(5), 809–822.
21 D. Cossa and M. Coquery, The Mediterranean Mercury Anomaly, a Geochemical or a Biological Issue, in *Handbook of Environmental Chemistry, Review Series in Chemistry*, ed. A. Saliot, The Mediterranean, 2004, vol. 5, 39p.
22 L. Lambertsson and M. Nilsson, Organic material: the primary control on mercury methylation and ambient methyl mercury concentrations in Estuarine sediments, *Environ. Sci. Technol.*, 2006, **40**, 1822–1829.
23 N. Ogrinc, J. Kotnik, V. Fajon, M. Monperrus, D. Kocman, K. Vidimova, D. Amouroux, S. Žižek and M. Horvat, Distribution of mercury and methylmercury in sediments of the Mediterranean sea, *Mar. Chem.*, 2007, **107**, 31–48.
24 K. Le Donne and S. Ciafani, Monitoraggio dell'inquinamento atmosferico da mercurio nei principali impianti cloro-soda italiani, *Ing. Ambientale*, 2008, **37**, 45–52.
25 Istituto Centrale Per La Ricerca Scientifica E Tecnologica Applicata Al Mare (ICRAM), *Elaborazione e valutazione dei risultati della caratterizzazione ambientale della Rada di Augusta—aree prioritarie ai fini della progettazione degli interventi di messa in sicurezza di emergenza—Sito di interesse nazionale di Priolo*, BoI-Pr-SI-PR-Rada di Augusta-01.04, 2005, 92p.
26 E. Romano, L. Bergamin, M. G. Finoia, M. Celia Magno, A. Ausili and M. Gabellini, The Effects of Human Impact on Benthic Foraminifera in the Augusta Harbour (Sicily, Italy), in *Integrated Coastal Zone Management*, ed. E. Moksness, E. Dahl and J. Støttrup, Wiley-Blackwell, Chichester, 2009, pp. 97–115.
27 R. Rajar, M. Četina, M. Horvat and D. Žagar, Mass balance of mercury in the Mediterranean Sea, *Mar. Chem.*, 2007, **107**, 89–102.
28 R. Di Leonardo, A. Bellanca, L. Capotondi, A. Cundy and R. Neri, Possible impacts of Hg and PAH contamination on benthic foraminiferal assemblages: an example from the Sicilian coast, central Mediterranean, *Sci. Total Environ.*, 2007, **388**, 168–183.
29 R. Di Leonardo, A. Bellanca, M. Angelone, M. Leonardi and R. Neri, Impact of human activities on the central Mediterranean offshore: evidence from Hg distribution in box-core sediments from the Ionian Sea, *Appl. Geochem.*, 2008, **23**, 3756–3766.
30 Istituto Centrale Per La Ricerca Scientifica E Tecnologica Applicata Al Mare (ICRAM), *Progetto preliminare di bonifica dei fondali della rada di Augusta nel sito di interesse nazionale di Priolo—Elaborazione definitiva*, BoI-Pr-SI-PR-Rada di Augusta-03.22, 2008, 182p.
31 F. Budillon, L. Ferraro, T. S. Hopkins, M. Iorio, C. Lubritto, M. Sprovieri, A. Bellonia, F. Marzaioli and R. Tonielli, Effects of intense anthropogenic settlement of coastal areas on seabed and sedimentary systems: a case study from the Augusta Bay (Southern Italy), *Rendiconti online Società Geologica Italiana*, 2008, **3**, 142–143.
32 P. Scandone, E. Patacca and R. Radoicic, Mesozoic and Cenozoic rocks from Malta escarpment (central Mediterranean), *AAPG Bull.*, 1981, **65**(7), 1299–1319, DOI: 10.1306/03B5949F-16D1-11D7-8645000102C1865D.
33 M. Giani, M. Gabellini, D. Pellegrini, S. Costantini, E. Boccaloni and R. Giordano, Concentration and partitioning of Cr, Hg and Pb in sediments of dredge and disposal sites of the northern Adriatic sea, *Sci. Total Environ.*, 1994, **158**, 97–112.
34 G. Matheron, *The Theory of Regionalized Variables and its Application*, Ecole Nationale Supérieure des Mines de Paris, Paris, 1971.
35 European pollutant emission register, http://www.eper.sinanet.apat.it/site/it IT/Registro_INES/Ricerca_per_complesso_industriale/ricercaINES.html.
36 S. A. Strode, L. Jaegle, N. E. Selin, D. J. Jacob, R. J. Park, R. M. Yantosca, R. P. Mason and F. Slemr, Air–sea exchange in

the global mercury cycle, *Global Biogeochem. Cycles*, 2007, **21**, GB1017, 12p.
37 M. E. Andersson, K. Gårdfeldt, I. Wängberg, F. Sprovieri, N. Pirrone and O. Lindqvist, Seasonal and daily variation of mercury evasion at coastal and off shore sites from the Mediterranean Sea, *Mar. Chem.*, 2007, **104**, 214–226.
38 C. Gobeil and D. Cossa, Mercury in sediments and sediment porewater in the Laurentian Trough, *Can. J. Fish. Aquat. Sci.*, 1993, **50**(8), 1794–1800.
39 C. Gagnon, E. Pelletier and A. Mucci, Behaviour of anthropogenic mercury in coastal marine sediments, *Mar. Chem.*, 1997, **59**, 159–176.
40 W. X. Wang, I. Stupakoff, C. Gagnon and N. S. Fisher, Bioavailability of inorganic and methylmercury to a marine deposit feeding polychaete, *Environ. Sci. Technol.*, 1998, **32**(17), 2564–2571.
41 R. Rajar, D. Žagar, M. Četina, H. Akagi, S. Yano, T. Tomiyasu and M. Horvat, Application of three-dimensional mercury cycling model to coastal seas, *Ecol. Modell.*, 2004, **171**, 139–155.
42 T. Tomiyasu, A. Matsuyama, T. Eguchi, K. Marumoto, K. Oki and H. Akagi, Speciation of mercury in water at the bottom of Minamata Bay, Japan., *Mar. Chem.*, 2008, **112**, 102–106.
43 S. Covelli, J. Faganeli, C. De Vittor, S. Predonzani, A. Acquavita and M. Horvat, Benthic fluxes of mercury species in a lagoon environment (Grado lagoon, Northern Adriatic Sea, Italy), *Appl. Geochem.*, 2008, **23**(3), 529–546.
44 K. Y. Choe, G. A. Gill, R. D. Lehman, S. Han, W. A. Heim and K. H. Coale, Sediment-Water exchange of total mercury and monomethyl mercury in the San Francisco bay-Delta, *Limnol. Oceanogr.*, 2004, **49**(5), 1512–1527.
45 M. H. Bothner, R. A. Jahnke, M. L. Peterson and R. Carpenter, Rate of mercury loss from contaminated estuarine sediments, *Geochim. Cosmochim. Acta*, 1980, **44**, 273–285.
46 ENVIRON, *Valutazione di un modello concettuale del sito e descrizione dei processi dei sedimenti e delle condizioni geochimiche nel porto industriale della Rada di Augusta*, Sicilia, Italia, 2008, 45p.
47 D. M. Di Toro, *Sediment Flux Modeling*, Wiley, New York, 2001, 624p.
48 D. M. Di Toro and J. J. Fitzpatrick, *Chesapeake Bay Sediment Flux Mode, Technical Report*, Environmental Laboratory, US Army Engineer Waterways Experiment Station, 2003.
49 P. Malanotte-Rizzoli, B. B. Mancab, M. Ribera D'Alcalà, A. Theocharisd, A. Bergamasco, D. Bregant, G. Budillon, G. Civitares, D. Georgopoulos, A. Michelato, E. Sansone, P. Scarazzato and E. Souvermezoglou, A synthesis of the Ionian Sea hydrography, circulation and water mass pathways during POEM phase I, *Prog. Oceanogr.*, 1997, **39**, 153–204.
50 P. F. J. Lermusiaux and A. R. Robinson, Features of dominant mesoscale variability, circulation patterns and dynamics in the Strait of Sicily, *Deep-Sea Res., Part I*, 2001, **48**, 1953–1997.
51 E. Napolitano, G. Sannino, V. Artale and S. Marullo, Modelling the baroclinic circulation in the area of the Sicily channel: The role of stratification and energy diagnostics, *J. Geophys. Res.*, 2003, **108** (C7), 3230, DOI: 10.1029/2002JC001502.
52 F. Raffa and T. S. Hopkins, Circulation and water mass structure over a narrow shelf, Augusta Gulf (Sicily), *Chem. Ecol.*, 2004, **20**(1), 249–266.

