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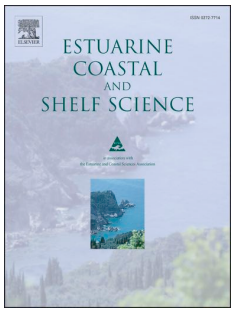

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Fluxes and the mass balance of mercury in Augusta Bay (Sicily, southern Italy)

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Abstract

The flux (Φ) of mercury (Hg) at the sediment-seawater interface was investigated in Augusta Bay (southern Italy) where uncontrolled industrial discharge from one of the most important chlor-alkali plant in Europe has caused significant negative effects on the environment. Hg fluxes were measured by the deployment of in-situ benthic chamber. The obtained value of 1.3 kmol y^{-1} clearly emphasizes the role of the sediments as source of Hg for the overlying water column. Moreover, Hg concentrations in the outflowing bottom waters were measured to estimate the export of this pollutant from Augusta Bay to the open sea. The calculated value of 0.54 kmol y^{-1}, corresponding to ~4% of the anthropogenic input of Hg from coastal point/diffuse sources to the Mediterranean Sea (12.5 kmol y^{-1}; Rajar et al. 2007; UNEP-MAP 2001), assigns this area a crucial role in the Hg inventory of the entire Mediterranean basin. Finally, a consistent and robust mass balance for Hg in Augusta Bay was provided by combining the obtained data with Hg fluxes at seawater-atmosphere interface.

Keywords: mercury pollution, benthic fluxes, mass balance, Mediterranean Sea.

1. Introduction

The need to monitor mercury in coastal marine environments is an issue of great concern, especially where the anthropogenic impact is significant. Coastal areas play a key role in the global cycle of this element (Mason et al., 1994), not only as a natural sink for terrestrially-derived Hg (Whalin et al., 2007), but also as a potential source of methylmercury in the ocean (Mason and Benoit, 2003). Despite the crucial importance of the coastal and shelf areas in the Hg biogeochemical cycle, few papers have focused on the role played by these regions as pollutant sources for the open sea, minimizing the role of Hg outflows in performing oceanic-scale mass balance (e.g., Cossa and Coquery, 2004; Rajar et al., 2007).

Augusta Bay, situated on the eastern Sicily (Southern Italy), is one of the most polluted area in the Mediterranean Sea, because of uncontrolled discharges (since1950s) from petrochemical plants. In particular, the southernmost part of Augusta Bay hosted, from 1958 to 2005, an important mercury-cell chlor-alkali plant (Le Donne and Ciafani, 2008) which discharged without treatments in the bay, until restrictions were imposed by Italian law in the late 1970s (Bellucci et al., 2012). Documented effects of this indiscriminate discharges include: extremely high Hg concentrations in the bottom sediment (up to 770 $mgkg^{-1}$) (ICRAM, 2008; Environ, 2008; Sprovieri et al., 2011), significant Hg evasion fluxes to atmosphere (~10 g d^{-1}) (Bagnato et al., 2013) and a potential risk associated with local fish consumption (Ausili et al., 2008; Bonsignore et al., 2013). Furthermore, Bonsignore et al. (2015) measured Hg isotopes to trace transfer mechanisms of this toxic element from sediment to the fish compartment and eventually to the resident population in Augusta area, for which alarming increases in congenital malformations, abortions and mortality rates were recorded (Madeddu et al., 2003). Recently, Sprovieri et al. (2011) used indirect calculations to implement a Hg mass balance for the polluted Augusta Bay and estimated an outflow of ~0.16 Kmol y^{-1} to the open sea, which corresponds to ~1% of the Hg anthropogenic input to

Mediterranean sea from point and diffuse sources (12.5 Kmol y^{-1}; Rajar et al., 2007). This result emphasizes the role played by Augusta Bay as source of mercury at Mediterranean scale.

Here, we present a revised and more quantitatively robust mass balance of Hg in Augusta Bay based on unprecedented information obtained by benthic chamber experiments, measurements of Hg in outflowing seawater and evasional fluxes to atmosphere (Bagnato et al., 2013). The study offers the valuable opportunity to provide a comprehensive vision of the geochemical cycle of Hg in Augusta Bay, with particular attention paid to the benthic fluxes. It also explores the role played by Augusta bay as potential Hg point source for the Mediterranean sea. In fact, owing to its geographical location, the outflowing shelfwater is immediately intercepted by the surface Atlantic Ionian Stream (AIS) and mixed with the main gyres of the eastern Mediterranean Sea, thus representing a risk in terms of large-scale marine system.

2. Study area

Augusta Bay is a natural semi-enclosed marine area of ~23.5 km^2, located in Eastern Sicily (Ionian Sea, southern Italy), delimited in the northern sector by the town of Augusta and closed to South and East by artificial dams built in the early ’60s (Fig. 1). It hosts one of the most important harbour of the Mediterranean Sea characterized by an intensive ship traffic. Two main mouths allow connection with the open sea: Scirocco (300 m wide and 13 m deep) and Levante inlets (400 m wide and 40 m deep). The exchanges with open sea are mainly driven by tidal fluctuations and, consequently correlated with the entry/exit of tidal flows and relative amplitudes. The input water at Levante mouth is characterized by a mean speed of 18 cm s^{-1} (depth= 0-5 m) at the surface and 7 cm s^{-1} at the bottom. (depth= 30-40 m). The input water circulation flows northward, parallel to the dam, while, the output current flows in opposite directions, with speeds of 5-6 cm s^{-1} (depth= 5-30 m) The Scirocco mouth is mainly affected by outflowing water, which goes parallel to the coastline with moderate speeds (5-6 cm s^{-1}). Finally, the northern part of the bay is scarcely affected by active

currents (ICRAM, 2008; Sprovieri et al., 2011). Recent bathymetric surveys carried out by Budillon et al. (2008), showed a very narrow shelf develops down to 100–130 m with a mean gradient of about 1.0° and a steep slope characterized by a dense net of canyons dropping to the deep end of the Ionian basin (Fig. 1). As consequence of the industrial development, which has affected the area since 1960s, a wide range of pollutants has been introduced into Augusta Bay. In particular, high levels of Hg contamination resulted by the activities of the chlor-alkali plant, which discharged without treatments until the 1970s, when a demercurization plant and waste treatments became operative (Bellucci et al., 2011). Owing to the high state of environmental degradation, this area was included in 2002 in the National Remediation Plan by the Italian Environmental Ministry.

3. Materials and sampling strategy

The sampling strategy included the collection of seawater and sediment, as well as the placement of a benthic chamber at the bottom of the bay to estimate the Hg fluxes at the sediment-seawater interface (Fig. 1, Tab. 1). In May 2011, seawater samples were collected from the whole study-area (Fig. 1a), while sediment sampling stations (Fig. 1b) were selected in order to cover the range of Hg concentration previously reported from other studies (ICRAM, 2008; Environ, 2008; Sprovieri et al., 2011). Hg distribution obtained from the analysis of these samples drove the benthic chamber deployment performed in September 2011 and June 2012 (Fig. 1c), in order to measure fluxes from sediments characterized by different Hg pollution levels. In June 2012, also seawater and sediment were sampled in the same stations where benthic chamber experiments were performed (Fig. 1 a, b, c). Finally, in February 2012, seawater samples were collected outside the bay in order to investigate the export of Hg to open sea (Fig. 1a).

3.1 Seawater collection

Seawaters were collected from 18 stations inside and 4 outside the bay, at three different depths (surface, mid-water and bottom) with a Niskin bottle rosette or a single Niskin bottle transported by

a scuba diver (Fig. 1a; Tab. 1). All of the samples were preserved in bottles, previously cleaned with HNO_3/HCl (10%) and rinsed with Milli-Q water (18.2 MΩ cm^{-1}). Samples were stored at -20°C until the analyses (Horvat et al., 2003). Measurements of temperature and salinity along the water column were obtained by multiparametric probe (CTD SBE 9plus).

3.2 Sediment sampling

Sediments were collected using a box-corer or a Plexiglas tube (length=30 cm; diameter=6 cm), manually inserted into the bottom sediment by a scuba diver (Tab. 1; Fig. 1b) and immediately stored at –20 °C until the analyses.

3.3 Benthic chamber

To calculate the Hg fluxes at the sediment-seawater interface, a benthic chamber was designed and assembled at the IAMC-CNR-Capo Granitola, where the base model proposed by Covelli et al. (1999, 2008) was modified. Briefly, a Plexiglas box-shape chamber (50x50x30 cm), open at the bottom side, was internally equipped with a stirring mechanism. This consisted of a rolling bar (30 cm long; 5 rpm speed) moved by an electromotor (12 V) located on the top of the chamber. A plastic skirt fitted outside the chamber controls its penetration into the sediment to a depth of 7.5 cm. Seawater from the benthic chamber was periodically sampled at discrete, consecutive temporal intervals (t=0, t= 1, t=4, t=6, t=10 and t=12 h) with a syringe inserted into a cap with a rubber pierceable septum. It was immediately transferred into acid-pre-cleaned vials and stored at T= -20°C until analyses.

4. Analytical methods

Analyses were performed at Geochemical Laboratory of IAMC-CNR - Capo Granitola. In order to minimize contamination, acid-cleaned laboratory materials and ultrapure grade reagents were used during sample preparation and analyses.

131

132 ***4.1 Seawater***

133 Total (THg) and dissolved Hg (DHg) in the seawater were determined using a direct mercury
134 analyzer (Milestone_DMA-80) (US-EPA 7473), after oxidation with a bromine monochloride
135 (BrCl) fresh solution (0.5 mL/100 mL sample) (US-EPA 1631). The DHg was determined after
136 sample filtration (0.45 μm), in seawater samples collected from the benthic chamber and outside the
137 bay. Blank and duplicate samples (about 20% of the of samples) were analyzed to assess detection
138 limit (d.l.= 1.9 ng L^{-1}; 3σ of the reagent blank), and reproducibility (better than 10%) of the method.
139 Accuracy was estimated by spiked samples analysis being the certificated value of the available
140 Reference Standard Material (BCR-579 Coastal Seawater) 1-2 orders of magnitude lower than
141 investigated analytical range. Obtained recoveries resulted to be between 85 and 110%.

142

143 ***4.2 Sediment***

144 Once defrosted, extruded from the liner, sediment cores were sectioned at 1-3 cm intervals with a
145 stainless steel band saw. About 3.5 g of wet sediment were picked from each slide for the grain size
146 analyses, performed with a laser granulometer (Horiba Partica LA-950V2) after treatment with
147 H_2O_2 (2:8) and Milli-Q water to remove organic material and cemented salts (Romano and
148 Gabellini, 2001). The remaining sediment were dried at 35°C and powdered using an agata mortar.
149 About 10 mg of dry sediment were loaded into specific nickel boats and analyzed by DMA-80 for
150 Hg analysis (US-EPA 7473). A Reference Standard Material (PACS-2 Marine sediment, NRCC)
151 was analyzed to assess accuracy (estimated to be ~7%) and precision (routinely better than 6%;
152 RSD%, n= 3). Finally, duplicate samples (about 20% of the total samples) were analyzed to
153 estimate the reproducibility (better than 7%). Total organic-carbon (TOC) was determined in bulk
154 sediment by a Thermo Electron Flash EA 1112 after elimination of all the carbonate (with HCl 1M
155 for 24 h at $T_{ambient}$ and drying at 60°C) (Nieuwenhuize et al., 1994).

156

5. Results

5.1 Seawater

Total and dissolved mercury concentrations measured in the seawater sampled within and outside Augusta Bay are reported in Table 2. The [THg] in the internal seawater vary widely from <1.90 (<d.l.) to 129 ngL^{-1} (Tab. 2), with an evident north-south increasing trend (Fig. 2).

The highest [THg] occurred in south-western area (S11-S25), ranging between 3.3 and 129 ngL^{-1} in the 10-20m depth interval, between 2.27 and 127 ngL^{-1} in the deep waters (<10m from bottom) and from <1.90 to 26.3 ngL^{-1} in the shallow waters (>20m from bottom) (Fig. 2).

It is noteworthy that extremely high levels of THg were measured in S23, at the bottom ([THg]= 57.8 ngL^{-1}), and in S17, at middle and deep depths ([THg]= 129 and 127 ngL^{-1} respectively) (Tab. 2). Lower concentrations (average= 12.0±7.00 ngL^{-1}) were found in the northern stations (S1-10) (Tab. 2). Furthermore, an increasing trend of [THg] with depth was highlighted along the seawater column, where, systematically, the surface waters show the lowest THg content (average= 11.1±8.49 ngL^{-1}), the deep waters have the highest one (average= 25.5±29.3 ngL^{-1}) and the middle waters have intermediate THg levels (average= 20.1±29.1 ngL^{-1}). The [THg] and [DHg] measured in seawater samples outside the bay (S26-29) varied between 2.62 and 11.9 ngL^{-1} and between <d.l. and 5.55 ngL^{-1}, respectively. Once again, an increasing trend of [THg] with depth was measured. In particular, the highest values (THg= 11.0 and 11.9 ngL^{-1}; DHg= 5.55 ngL^{-1}) were measured in the bottom seawaters (Tab. 2).The range of temperature measured inside the bay is relatively wide (from 16.6 to 20.4°C), with warmer surface water (T range= 19.0-20.4°C) and colder deep water (T range= 16.6-20.2°C). The low temperatures observed in the eastern part of the bay (S25, S13) are due to the input of relatively colder water from the open sea, with measured values ranging from 13.9 to 15.2 °C (Tab. 2). Salinity ranges from 36.7 to 39.0 *psu* inside and between 37.9 and 38.9 *psu* outside the bay. The lower values recorded inside the bay are probably due to inputs of freshwater or sewage from land (Tab. 2).

5.2 Sediment

Grain size, TOC and [Hg] measured in the sediment are reported in Figure 3 (a, b, c, respectively) and Appendix I.

Almost all of the analyzed samples consist of silt (more than 50%) and clay (32-45%), whereas the sandy fraction represents a small percentage (~10%). Only the S19 core is sandy (~70%) and contains small amounts of silt (~17%) and clay (~13%). The calculated sorting parameter (ranging from 4.8 to 12.2 μm) is indicative of a low energy environment, where the slow current circulation affects the poor size selection of the sediment (Fig. 3a).

All samples show high TOC (from 1.58 to 4.26%), thus suggesting relatively high burial/preservation of organic matter in the sediment. In the southern S21, the values range widely from 1.58 to 3.45% (average= 2.32±0.50%) with an irregular distribution along the core, characterized by an evident peak (3.45%) at 14-16 cm. In the S15 core, the TOC-depth profile is quite constant except for two peaks at 2-4 cm (2.85%) and 20-22 cm (4.26%) (average= 2.38±0.68%). The lowest mean value (2.27±0.11%) was measured in the northern station (S7), where TOC show a steady trend with depth (Fig. 3b).

The measured [THg] varies widely (from 1.77 to 55.3 $mgKg^{-1}$) (Fig. 3b). The highest values were found in the southern stations, specifically in the intermediate part (6-21 cm) of the core S14, with [THg] ranging between 20.8 and 39.5 $mgKg^{-1}$, and along the core S21, where the values vary between 19.0 and 55.3 $mgKg^{-1}$, in the interval from 4 to 30 cm). Moreover, the concentration-depth profiles in cores S14 and S21 are characterized by a marked peak between 12 and 16 cm, whereas nearly steady trends were measured in the remaining cores. The lowest values were found in the northern stations, with average concentrations of 6.33±0.91 $mgKg^{-1}$ in S7, 6.15±1.54 $mgKg^{-1}$ in S8; and in the sandy S19 core (average= 7.81±1.66 $mgKg^{-1}$) collected from the southern area (average= 7.81±1.66 $mgKg^{-1}$). Finally, intermediate values were measured in S15 (average= 12.5±2.66 $mgKg^{-1}$) and S16 (average= 16.2±1.66 $mgKg^{-1}$) (Fig. 3c).

5.3 Benthic fluxes

The DHg content in the seawater at the sediment-seawater interface increased with time at all stations (Appendix II, Fig. 4). Specifically, the increasing trend was constant for the entire incubation period (0-10/12h) in chambers 18 and 21, while in the other stations the DHg content exhibited a major increase in the first hour (0-1h), but was almost constant during the time interval that followed (1-10/12h) (Fig. 4). The mercury fluxes across the sediment-seawater interface were calculated on the basis of the best fit curve "concentration *vs* time", according to the following equation (Santschi et al., 1990) (1):

$$\phi Hg = \left(\frac{\delta C}{\delta t} \times \frac{V}{A} \right) \quad (1)$$

where:

$\delta C/\delta t$ = variation of the Hg concentration over time (ng L^{-1} h^{-1}).

V= volume of the benthic chamber (57.5 L).

A = cover area of the sea-bottom (0.25 m^2).

Finally, the obtained results were normalized to 24h. The mercury fluxes per day calculated in the northern area were very comparable in the neighboring S7 and S9 (22.7 and 22.6 µg m^{-2} d^{-1}, respectively) (Fig. 4). Conversely, in the southern area, significant differences among the stations were observed . In particular, S15 and S22 had the highest values (92 and 56 µg $m^{-2}d^{-1}$, respectively), while relatively low flux (8.7 µg $m^{-2}d^{-1}$) were estimated for S18, despite the closeness to S21, where a higher flux of 20.5 µg $m^{-2}d^{-1}$ was recorded (Fig. 4). The calculated fluxes were extended to a yearly estimation and then over the entire area using the territorial distribution model proposed by Aurenhammer (1991) (Voronoi Polygons method). The estimated fluxes amounted to 1.1 kmol y^{-1} in September 2011 (0.22 t y^{-1}) and 1.4 kmol y^{-1} (0.29 t y^{-1}) in June 2012.

6. Discussion

The [Hg] measured in Augusta Bay sediment are extremely elevated (Fig. 3c), being 1-2 orders of magnitude higher than the Mediterranean background values (0.04-0.17 $mgKg^{-1}$) (e.g., Donazzolo et al., 1981; Ogrinc et al., 2007). They are also comparable with the values (4.06 and 79.0 mg Kg^{-1}) reported for sediment of other coastal areas affected by relevant industrial or mining activities (e.g., Baldi and Bergagli, 1984; Covelli et al., 2001, 2008, 2011; Emili et al., 2012). The higher concentrations, measured in the southern stations, can be attributable to industrial input (~2.1 kg y^{-1}; value reported by the European Pollutant Emission Register) and to the proximity of the most important chemical and petrochemical plants (Syndial Priolo Gargallo, ESSO, ERG, etc.). In particular, the chlor-alkali plant, is considered to have been the main Hg source in the bay (Di Leonardo et al., 2007; ICRAM, 2008; Sprovieri et al. 2011; Bellucci et al., 2012), with an average discharge of about 260 kg y^{-1} of Hg estimated between early-1960 and late-1970 (Colombo et al., 2005). However, in Augusta Bay, effects of re-suspension due to the intensive ship traffic, combined with relevant dredging activities occurred since 1960s, make the historical reconstruction of industrial contaminant inputs very difficult to be achieved without a specific integrated approach (Cundy et al., 2003; Bellucci et al., 2012). Concentrations measured in the studied cores are in good agreement with the Hg areal distribution in surface sediment reported by Sprovieri et al. (2011), which subdivided Augusta Bay in two geographical sectors characterized by significantly different levels of contamination: i) a southern sector ([Hg] median value=23.8 $mgKg^{-1}$) affected by chemical and petrochemical plants activity and ii) a northern sector ([Hg] median value= 1.1 mg Kg^{-1}) affected by municipal waste discharge. The only exception is represented by S19 core, characterized by Hg contents lower than those found in the neighboring stations. It is probably due to its specific sandy grain-size composition (Fig. 3a) responsible for a less Hg adsorbing capacity (Ravichandran, 2004). On the other hand, a positive correlation was found between [Hg] and finer grain-size fraction for S14 (r^2= 0.7) and S21 (r^2= 0.5), where specifically, the highest Hg levels correspond to the highest silt-clay percentages (92 and 95%) (Fig. 3 c, a). The high TOC values

measured (Fig. 3, Appendix I) are compatible with the disoxic/anoxic conditions measured at the bottom basin (average Eh~ -300 mV; ICRAM, 2008; Sprovieri et al., 2011) and possibly due to the state of semi-closed environment of the basin and the low energy hydrodynamics. Noteworthy, high contents of organic matter under reducing environmental conditions promote methylation processes, mediated by microorganisms, such as sulfate reducing bacteria (SRB), at water/sediments interface (e.g., Langer et al., 2001; Lambertsson and Nilsson 2006). Thus, bottom sediments in Augusta bay represent a potential source of methylmercury (MeHg) for the ecosystem which could also partially justify the high levels of Hg found in fish caught in the bay (Bonsignore et al., 2013, 2016).

.A significant statistical correlation (r^2= 0.71) between [THg] and TOC, was found in the core S21, where peaks of Hg corresponding to the highest TOC values (Fig. 3 c, b) occur. Conversely, no positive correlation was recorded in the other cores (S7, S15). The north-south positive gradient of [Hg] in the Augusta sediment is reflected in the spatial distribution of THg in seawater, with lower values recorded in the northern area and higher ones in the south (Fig. 2). Noteworthy, an evident [THg] vertical increasing trend was observed along the water column (Fig. 2, Tab. 2), with the lowest concentrations measured in the surface layers, where the penetrating sunlight promotes the photoreduction and the subsequent volatilization of Hg^0 form (Fitzgerald and Clarkson, 1991; Bagnato et., 2013), and the highest values found close to the bottom, where resuspension events and Hg release from sediment probably affect the concentration of this pollutant in the overlying water column. In the marine environment, Hg is generally bound to sediment through: ion exchange, complexing or chelation with organic and inorganic ligands, sorption with Fe/Mn oxide-hydroxides or incorporation into mineral lattice (Ramamoorthy and Massalki, 1979). However, changes in physical-chemical parameters at the sediment-seawater interface, bioturbation, dredging activities and methylation, may result in remobilization and diffusion of the Hg in the water column (Covelli et al., 1999). In this study, benthic chamber experiments provided direct measurement of Hg fluxes from the sediment to the overlying seawater. The obtained values vary widely between 8.7 and 92 $\mu g\ m^{-2}d^{-1}$.These differences could be attributed to variable Hg concentrations in surface sediments

(Appendix I), where comparable physical-chemical conditions at the seawater-sediment interface and analogue Hg speciation occurs, as well-demonstrated by Oliveri et al. (2016, *in press*). The measured benthic fluxes are higher than those estimated for other contaminated areas (5 and 10 μg m^{-2} d^{-1}) (Bothner et al., 1980; Covelli et al., 1999; Boucher et al., 2011) and comparable with values reported by Covelli et al. (2008) for the highly-contaminated Grado Lagoon (37 and 77 μg m^{-2} d^{-1}). , The flux at the sediment-seawater interface estimated for the entire bay (1.3±0.1 kmol y^{-1}) is about two orders of magnitude higher than that of the evasion into the atmosphere (1.8 x10^{-2} kmol y^{-1}) (Bagnato et al., 2013). This could imply that a relevant part of the Hg released in seawater is recycled in the biogeochemical cycle (biota uptake, adsorption by suspended particulate matter, re-deposition) and/or outflows to the open sea. This latter hypothesis is supported by the anomalous Hg concentrations measured in the seawater outside Augusta Bay (Tab. 2), which were an order of magnitude higher than the Mediterranean background values (0.2-0.4 ng L^{-1}) (Cossa et al., 1997; Horvat et al., 2003; Kotnik et al., 2007; Rajar et al., 2007). This is in agreement with the data reported by Fantozzi et al., (2012), which measured unusual Hg contents in seawater out Augusta Bay (4.8 and 18 ngL^{-1}) and argued that the water circulation in the Strait of Sicily moves polluted masses from Augusta Bay eastwards. Moreover, Sprovieri et al. (2011) speculated that the effects of the meso-scale circulation of the Ionian Sea, together with a narrow shelf and a steep slope off Augusta Bay (Budillon et al., 2008) (Fig. 1), create a high potential risk of Hg contamination of the Mediterranean basin. This evidence calls for an appropriate estimate of the possible outflow of this pollutant from Augusta Bay to the open sea. To this aim, we took in account the DHg concentrations measured in the bottom water just outside Scirocco and Levante mouths (5.6 and 3.6 ng L^{-1}, respectively; Tab. 2) and the associated relative outputs of seawater (2.34 x 10^{13} kg y^{-1}), as reported by Sprovieri et al. (2011). Thus, the estimated Hg outflow resulted to be 0.54 kmol y^{-1}. This value corresponds to ~4% of the anthropogenic input of Hg from coastal point/diffuse sources to the Mediterranean Sea (12.5 kmol y^{-1}; Rajar et al. 2007; UNEP-MAP 2001), and definitively emphasizes the role played by Augusta Bay as a crucial "point source" at the basin scale.

Mass balance of Hg in Augusta Bay

A steady-state mass balance for mercury, calculated to explore the geochemical cycle of this pollutant within the Augusta Bay, is here proposed. For this purpose, the Augusta Bay was basically considered as an ‘‘environmental compartment’’ with well-defined borders and constrained hydrodynamics. According to the basic scheme proposed by Sprovieri et al. (2011), we applied the following equation:

$$\mathbf{I+A+AD+R = O+D+V} \qquad (2)$$

where:

I = total Hg influx from the surface Mediterranean seawater
A= input of dissolved Hg from anthropogenic activities
AD= atmospheric Hg deposition
R= Hg re-suspension/release from the sediment
O= Hg outflow from the basin to the open sea
D= amount of Hg recycled into Augusta Bay (buried in sediment and/or accumulated in the biota)
V= Hg evasion into the atmosphere

The total seawater Hg influx value (I) was estimated using data reported by Kotnik et al. (2007),and corresponded to an average input of Hg from the Ionian Sea to Augusta Bay of about 3.12±0.94 x 10^{-2} kmol y^{-1}. The anthropogenic Hg input into the basin (A), including discharges from wastewater treatment facilities and industrial activities (*Erg, Syndyal, Esso*) was considered to be 6.2 x 10^{-2} kmol y^{-1} (value reported by the European pollutant emission register for the year 2005). AD and V corresponded to the values reported by Bagnato et al. (2013) (0.42 x 10^{-2} kmol y^{-1} and 1.7±0.02 x 10^{-2} kmol y^{-1}, respectively). Finally, O and R are the values measured in this study, which correspond to the Hg outflow from the bay to the open sea (0.54±0.08 kmol y^{-1}), and the Hg flux from the sediment to the seawater (1.3±0.2 kmol y^{-1}), respectively. In particular, the last term represents the final result of Hg diffusion from porewater and desorption from re-suspended of

organic/inorganic particles. Thus, the Hg recycled (re-deposited and/or accumulated in the biota as MeHg) into the bay (D) results to be 0.84±0.22 kmol y^{-1}, which represents from ~45 to 75% of the total input of Hg in the Augusta Bay. while the remaining part escapes into atmosphere (1-2%) and outflows to open sea (average ~40%). This means that the Augusta Bay plays an important role in recycling and exporting of mercury into the Mediterranean Sea and represents a relevant point source for that system.

This study definitively states how strong interlinks between contaminants behaviour and ocean dynamics drive the specific control of point sources on widespread distribution of pollutants. In particular, this offers a good science-driven case for an appropriate conceptual approach to the Marine Strategy Framework Directive (2008/56/EC), which specifically states that it should be possible to determine how to keep the pressure of human activities within levels compatible with the preservation or restoration of a Good Environmental Status in the Mediterranean sea, from 2020 onwards.

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Figure captions:

Figure 1: Sampling location of the seawater (a), sediment (b) and benthic chamber (c) in the Augusta Bay.

Figure 2: Map of [THg] distribution in seawaters collected during May 2011; a) 0-10m from the bottom; b) 10-20m from the bottom; c) 20m from the bottom up to surface. Maps were created through3D block kriging and were themed on the "natural breaks" method.

Figure 3: Profile of TOC (a), [Hg] (b) and grain size composition (b) along the collected cores.

Figure 4: Concentration of DHg *vs*. time during the benthic chamber experiment.

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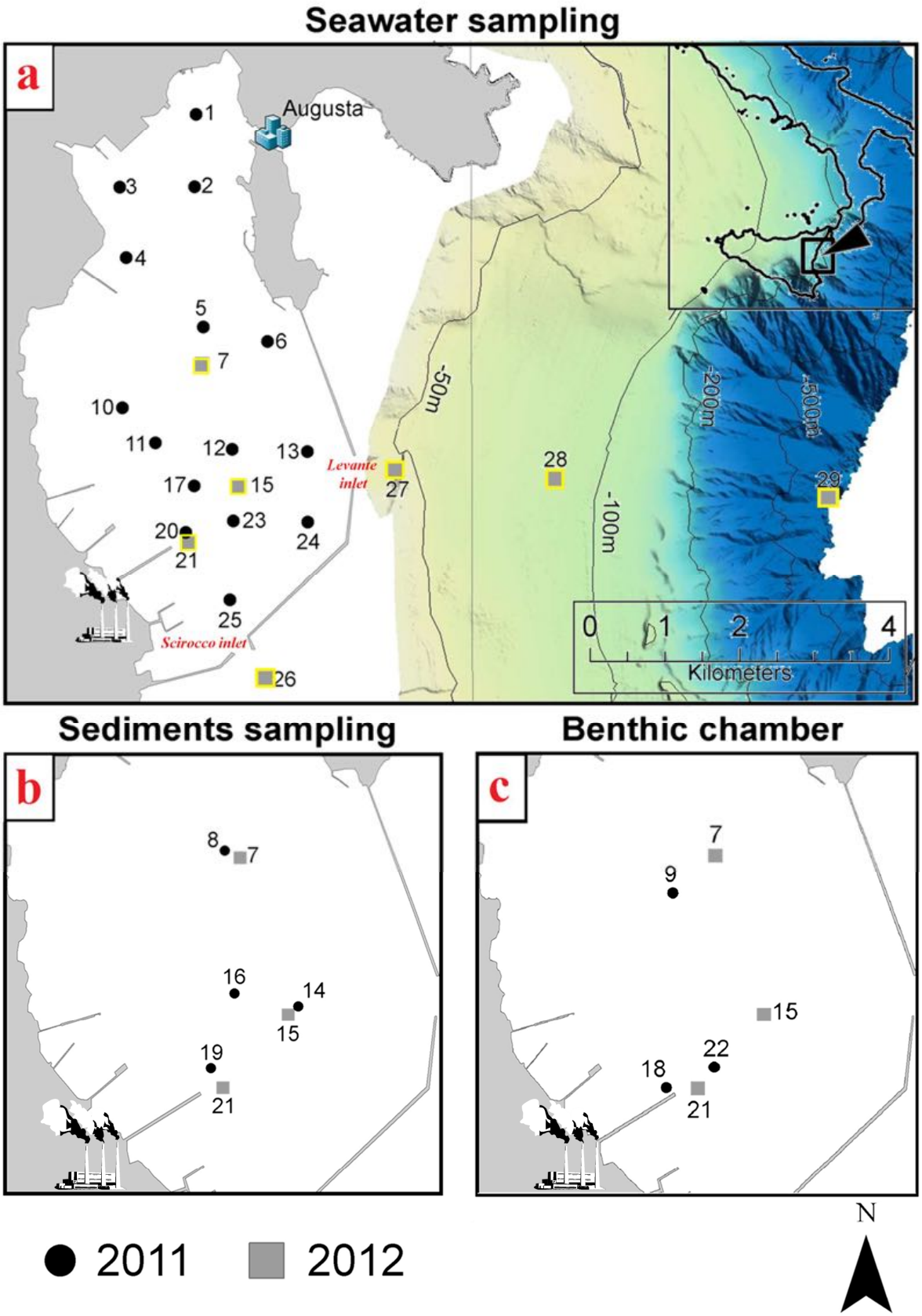
Table 1: Details of the sampling performed in Augusta Bay.

Sampling	Vessel	Period	Station			Bottom depth (m)	Method of sampling
				Lat.	Long.		
Seawaters	N/O G. Dallaporta	23-26/05/11	1	37°14.392N	15°12.537E	14.0	Niskin
			2	37°13.864N	15°12.519E	16.0	
			3	37°13.863N	15°11.845E	11.0	
			4	37°13.353N	15°11.902E	8.00	
			5	37°12.849N	15°12.595E	20.0	
			6	37°12.743N	15°13.176E	17.0	
			10	37°12.267N	15°11.863E	22.0	
			11	37°12.009N	15°12.161E	22.0	
			12	37°11.961N	15°12.855E	27.0	
			13	37°11.943N	15°13.536E	32.0	
			17	37°11.696N	15°12.512E	24.0	
			20	37°11.363N	15°13.536E	21.0	
			23	37°11.445N	15°12.434E	22.0	
			24	37°11.434N	15°13.536E	21.0	
			25	37°10.871N	15°12.833E	16.0	
	N/O Urania	02/02/12	26	37°10.310N	15°13.148E	17.0	Niskin
			27	37°11.807N	15°14.328E	42.0	
			28	37°11.742N	15°15.767E	85.0	
			29	37°11.604N	15°18.240E	679	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	22.8	Single Niskin bottle
			15	37°11.697N	15°12.917E	27.8	
			21	37°11.288N	15°12.459E	22.8	
Sediments	N/O G. Dallaporta	23-26/05/11	8	37°12.618N	15°12.473E	22.0	Box-corer
			14	37°11.745N	15°12.985E	28.0	
			16	37°11.818N	15°12.540E	27.0	
			19	37°11.399N	15°12.375E	21.0	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	22.8	Manual corer
			15	37°11.697N	15°12.917E	27.8	
			21	37°11.288N	15°12.459E	22.8	
Seawater at sediment-seawater interface	M/N L. Sanzo	19-21/09/11	9	37°12.369N	15°12.289E	22.0	Benthic chamber (syringe)
			18	37°11.294N	15°12.242E	21.0	
			22	37°11.406N	15°12.572E	24.0	
	M/N L. Sanzo	23-26/06/12	7	37°12.578N	15°12.583E	22.8	
			15	37°11.697N	15°12.917E	27.8	
			21	37°11.288N	15°12.459E	22.8	

Table 2: Total (THg) and dissolved mercury (DHg) concentration measured in the seawater column, inside and outside the bay.

	Sampling period	Station		Depth (m)	T (C°)	Salinity (psu)	THg (ngL^{-1})	DHg (ngL^{-1})
Inside Augusta Bay	23-26/05/2011	1	*Bottom*	11.2	18.0	38.0	17.8	
			Middle	6.20	18.4	38.0	9.17	
			Surface	1.40	20.4	38.0	9.17	
		2	*Bottom*	10.7	18.0	38.0	17.7	
			Middle	6.71	18.8	38.0	14.9	
			Surface	2.21	20.0	38.0	<d.l.	
		3	*Bottom*	8.40	18.1	38.0	30.0	
			Middle	4.60	19.7	38.0	12.0	
			Surface	2.26	20.3	38.0	<d.l.	
		4	*Bottom*	3.12	20.2	38.0	6.30	
			Surface	0.10	20.2	38.0	<d.l.	
		5	*Bottom*	15.9	17.7	38.0	17.7	
			Middle	9.20	18.5	38.0	7.10	
			Surface	1.00	19.8	38.0	9.20	
		6	*Bottom*	13.5	18.2	38.2	20.6	
			Middle	6.74	19.0	37.6	3.40	
			Surface	1.98	19.5	37.5	6.30	
		10	*Bottom*	19.2	17.4	38.0	14.9	
			Middle	9.50	18.8	38.0	15.9	
			Surface	1.00	20.0	39.0	4.30	
		11	*Bottom*	18.2	17.3	38.1	23.5	
			Middle	10.2	17.4	38.1	14.9	
			Surface	1.42	19.3	36.7	14.9	
		12	*Bottom*	23.4	17.0	38.1	19.3	
			Middle	13.5	17.9	37.8	3.37	
			Surface	1.63	19.4	37.1	17.7	
		13	*Bottom*	29.3	16.6	38.1	3.40	
			Middle	16.9	17.4	38.1	12.7	
			Surface	2.40	19.2	38.1	17.7	
		17	*Bottom*	21.9	17.2	38.1	127	
			Middle	11.5	18.0	38.0	129	
			Surface	1.20	19.1	38.0	26.3	
		20	*Bottom*	16.5	18.3	38.0	28.2	
			Middle	11.3	18.2	37.8	23.5	
			Surface	0.50	19.2	38.0	20.3	
		23	*Bottom*	20.6	16.9	38.1	57.8	
			Middle	11.2	18.0	38.0	20.6	
			Surface	2.40	19.0	38.0	23.4	
		24	*Bottom*	16.3	17.4	38.1	23.0	
			Middle	9.40	18.7	38.0	18.7	
			Surface	1.00	19.1	38.0	12.0	
		25	*Bottom*	12.7	17.7	38.1	34.9	
			Middle	7.30	18.5	38.0	32.0	
			Surface	1.60	19.3	38.0	22.6	
	23-26/06/2012	7	*Bottom*	21.0			1.80	
			Middle	11.5			9.90	
			Surface	1.00			<d.l.	
		15	*Bottom*	26.0			15.7	
			Middle	13.5			8.60	
			Surface	1.00			6.00	
		21	*Bottom*	22.0			18.1	
			Middle	11.5			14.9	
			Surface	1.00			1.00	

Outside Augusta Bay	**02/02/2012**	**26**	*Bottom*	8.00	11.1	5.55
			Surface	2.00	4.55	<d.l.
		27	*Bottom*	27.0	6.10	3.55
			Middle	16.0	4.80	<d.l.
			Surface	2.00	4.55	<d.l.
		28	*Bottom*	81.3	9.15	3.55
			Middle	45.3	5.42	<d.l.
			Surface	6.10	4.75	<d.l.
		29	*Bottom*	679	12.0	4.15
			Middle	375	6.15	5.55
			Surface	20.0	2.62	<d.l.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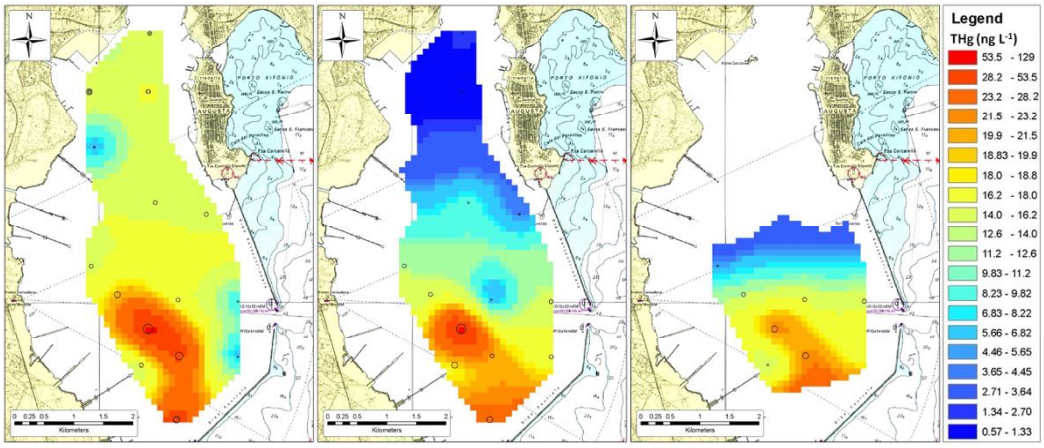

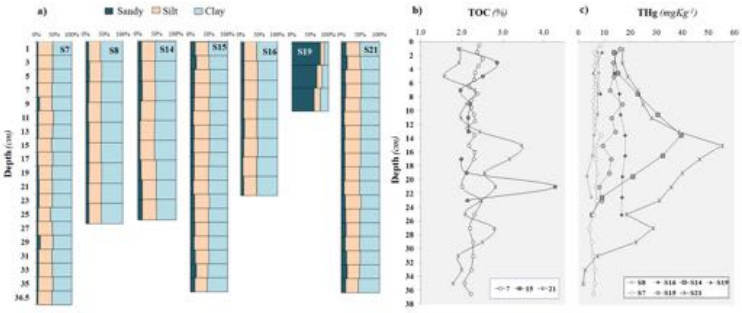

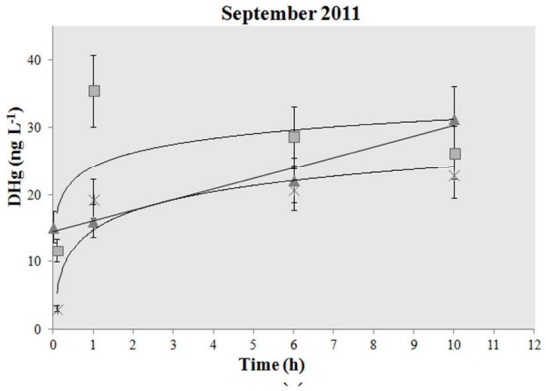

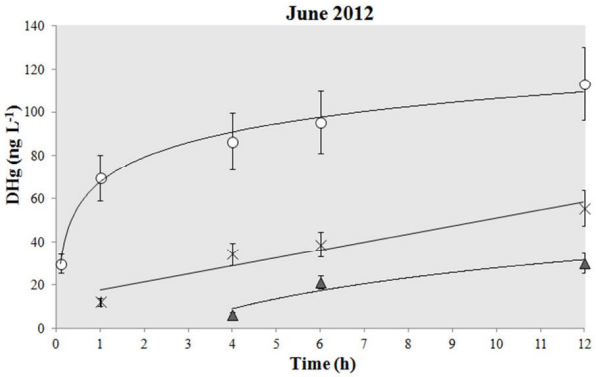

Station	Regression fit	Φ ($\mu g\ m^{-2}\ d^{-1}$)
▲S9	$Y=4.1\ln(x)+14.7; R^2=0.88$	23
✳S18	$Y=1.6x+14.6; R^2=0.97$	56
■S22	$Y=3.0\ln(x)+24.2; R^2=0.40$	8.7

Station	Regression fit	Φ ($\mu g\ m^{-2}\ d^{-1}$)
▲S7	$Y=20.6\ln(x)-19.7; R^2=0.91$	23
○S15	$Y=16.6\ln(x)+67.8; R^2=0.98$	92
✳S21	$Y=3.7x+13.8; R^2=0.92$	21