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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.

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 (since 1950s) 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 mg kg^{-1}) (ICRAM, 2008; Environ International Team, 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, 2016). 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

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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

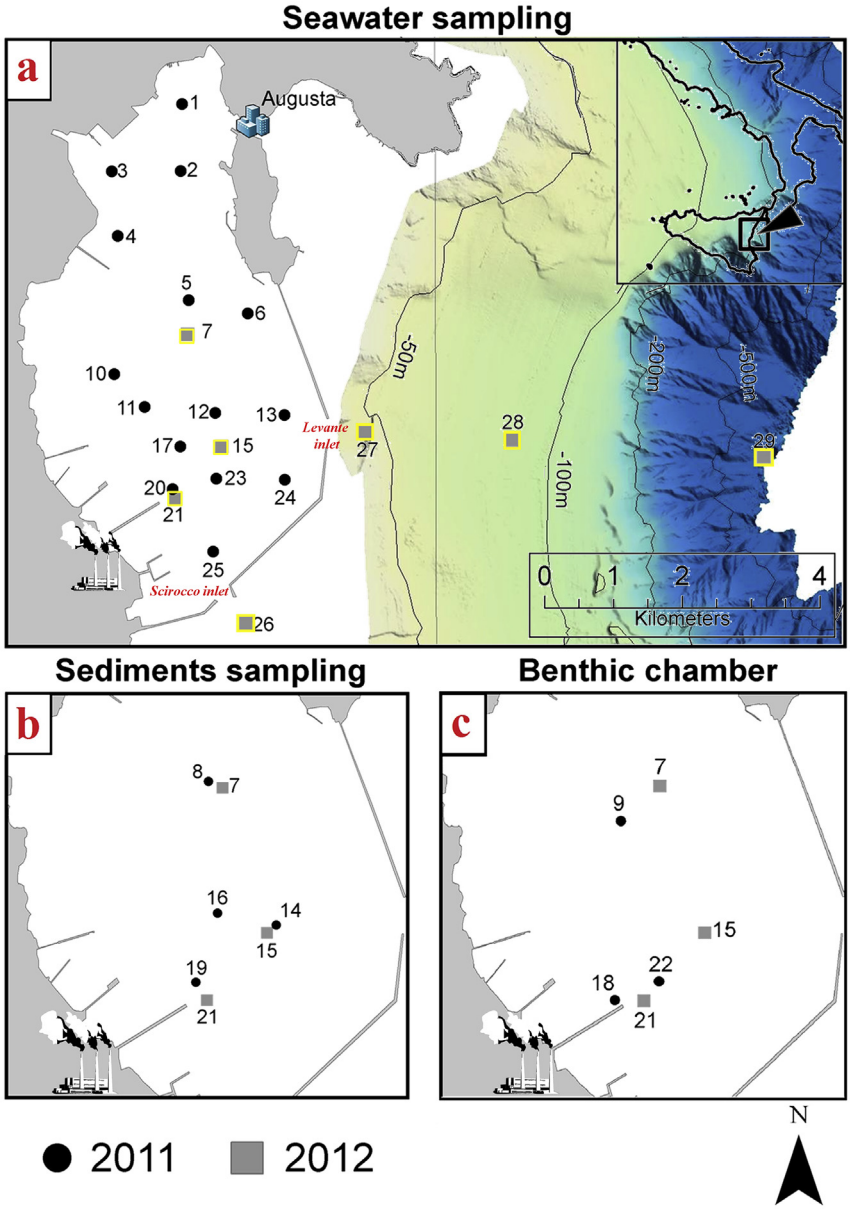

Fig. 1. Sampling location of the seawater (a), sediment (b) and benthic chamber (c) in the Augusta Bay.