

## Mobility of mercury in contaminated marine sediments: Biogeochemical pathways



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### ARTICLE INFO

#### Article history:

Received 11 March 2016

Received in revised form 24 June 2016

Accepted 5 July 2016

Available online 06 July 2016

#### Keywords:

Mercury

Hg bioavailability

Marine sediment

Pore water

Anaerobic sulphide oxidation

Augusta Bay

### ABSTRACT

The availability of dissolved inorganic mercury (DHg) in sediment pore water is a crucial step for the mechanisms of methylmercury (MeHg) generation in the aquatic system. The geochemical form of Hg in sediments and the redox-controlled microbial reactions taking place during *early diagenesis* regulate the pool of DHg and, consequently, the bioavailability of Hg for methylation. Here, we report new evidence on the biogeochemical mechanisms controlling the pool of DHg in sediment pore water from two box-cores collected from Augusta Bay (Sicily), a marine coastal zone heavily contaminated by chlor-alkali discharges. The content of the total Hg (THg) in the studied sediments ( $4.13 \div 22.2 \text{ mg Kg}^{-1}$ ) is largely present as an “immobile” phase, while the labile fractions account for minor percentages (<2%). Despite the predominance of Hg “immobile” forms, depth profiles of the pore water suggest relevant DHg production (up to  $226 \text{ ng L}^{-1}$ ) mainly in the deeper levels of the investigated sedimentary column. Specifically, most of the THg appears to be partially mobilized in the “Fe-Mn reduction” zone, as clearly suggested by significant correlations between DHg and dissolved Fe-Mn concentrations in the pore water. The irregular vertical distribution of  $\text{SO}_4^{2-}$ , with evident enrichment in the Fe-Mn reduction zone, could also indicate mechanisms of sulphate generation by sulphide oxidation. Specific microbial populations identified in the sediments appear dominated by chemolithoautotrophic sulphur oxidizing bacteria (SOB, genera *Sulfurovum* and *Thioalkalispira*) which could drive the microbial oxidation of sulphides and support, with effects of Mn-Fe oxide reduction, processes of Hg mobilization.

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### 1. Introduction

Coastal marine sediment is often a major repository of anthropogenic mercury (Hg), but biogeochemical reactions taking place during processes of *early diagenesis* can mobilize and definitively geochemically transform this pollutant (Bothner et al., 1980; Gagnon et al., 1997; 1996; Gobeil and Cossa, 1993; Jonsson et al., 2014) into more available and dangerous forms (e.g., the highly toxic methylmercury, MeHg; Barkay and Wagner-Döbler, 2005). The dynamics of Hg accumulation in marine sediment are primarily controlled by organic matter which is the most efficient Hg scavenger in the water column (Guentzel et al., 1996; Ravichandran, 2004), although iron and manganese oxides can also have an important role (Gobeil and Cossa, 1993; Feyte et al., 2010). When sediment undergoes redox changes because of organic matter mineralization (e.g., Froelich et al., 1979), the Hg bound to organic matter or Mn-Fe oxides can be released in pore water (Cossa and Gobeil, 2000; Gagnon et al., 1997; Gobeil and Cossa, 1993). In anoxic sulphuric sediments, the reaction between Hg and sulphide ( $\text{H}_2\text{S}$ ) can

lead to the precipitation of highly stable Hg-sulphides such as cinnabar (HgS, Huerta-Díaz and Morse, 1992; Revis et al., 1989). In this case, the factors controlling the solubility of Hg-sulphides will also influence the partitioning of Hg between sediment and pore water (Benoit et al., 1999a,b; Fitzgerald et al., 2007; Skjellberg, 2012). However, the excessive activity of sulphide ( $\text{HS}^-$ ) and/or the generation of zero-valent sulphur ( $\text{S}^0$ ) can promote HgS solubility and, consequently, induce effects of the mobility and availability of Hg in anoxic sediment (Jay et al., 2000; Paquette and Helz, 1997). This mechanism is responsible for the high concentrations of soluble mercury species that are often found in anoxic zones of the bottom sediment (Nakanishi et al., 1989; Fergusson, 1990). In order to adapt to the presence of mercury, microorganisms can affect the mobility of Hg in a variety of metabolic pathways (Barkay and Wagner-Döbler, 2005). It is widely recognized that sulphate reducing bacteria (SRB) can generate methylmercury (MeHg) in natural habitats like salt marshes and estuarine and freshwater sediment (Benoit et al., 2001a; Compeau and Bartha, 1985; Gilmour et al., 1992; King et al., 2000; Ranchou-Peyruse et al., 2009; Schartup et al., 2013). In sulphuric environments characterized by the precipitation of abundant Hg-sulphide (e.g. cinnabar), the polysulphide-induced solubilization of cinnabar can regulate availability for Hg methylation by SRB

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(Benoit et al., 2001b). In extreme environments such as deep sea vents and hot sulphuric springs, some microorganisms, e.g. sulphur oxidizing bacteria (SOB), outlive Hg through the sulphide oxidation of cinnabar deposits (Chatziefthimiou et al., 2007; Simbahan et al., 2005; Vetriani et al., 2005). Overall, the interactions between microbes and Hg-species facilitate the recycling of Hg and its bioavailability in the environment (Barkay and Wagner-Döbler, 2005).

This paper examines the main factors controlling the early diagenetic re-mobilization of Hg in sediments collected from the coastal marine area of Augusta Bay (eastern Sicily, Italy). In particular, the depth distributions of total Hg (THg) and the main parameters (grain size, mineralogy, and organic carbon) were analyzed in two sediment cores, to delineate the physico-chemical characteristics of the sediment matrix influencing Hg distribution in the Augusta Bay sediments. The sequential selective extraction (SSE) procedure was used to examine the main Hg solid-phases in the investigated sediment, with a view to evaluating the presence of mobile and potentially bioavailable species. Pore water chemistry was determined and analyzed for total Hg, Fe, Mn and  $\text{SO}_4^{2-}$  concentrations in order to study the predominant relationships between the release of Hg and the vertical change of the redox zone within the sediment. Pioneering microbiology exploration allowed us to identify the Hg-resistant microbial communities that inhabit the investigated environment and their pressure on Hg-remobilization in the Augusta Bay sediments.

## 2. Materials and methods

### 2.1. Study area

Augusta Bay occupies a coastal area of about 30 km<sup>2</sup> in eastern Sicily (southern Italy), and is one of the most industrialized and polluted areas in the Mediterranean Sea (Fig. 1a). The harbour area, delimited in the northern sector by the town of Augusta and closed to the south and east by artificial dams, is 8 km long and 4 km wide, with a mean water depth about of 15 m (ICRAM, 2008). Since the early 1960s, an important industrialization process has adversely affected the area (with

many chemical and petrochemical plants, oil refineries, etc.), but the most dangerous activity was caused by chlor-alkali plant with mercury cell operating from 1958 to 2003 (ICRAM, 2008). The uncontrolled discharge of huge amounts of Hg waste in the harbour led to significant contamination of the bottom sediment, particularly in the SW zone where the chlor-alkali plant was located (Fig. 1b) (Bellucci et al., 2012; Croudace et al., 2015; ICRAM, 2008; Sprovieri et al., 2011), with evident and recently documented risks for the ecosystem and human health (Bonsignore et al., 2015, 2013; Sprovieri et al., 2011;).

### 2.2. Sampling

Sediments were collected using a box-corer during a cruise expedition on the R/V "L. Dalla Porta" in May 2011 (Fig. 1b). One box-core was acquired from each site and immediately subsampled on board using 30-cm long polyethylene tubes. Specifically, four sub cores were recovered from each site and stored at  $-20\text{ }^{\circ}\text{C}$  until the geochemical analyses were conducted. Two sedimentary records were stored at  $+4\text{ }^{\circ}\text{C}$  for microbiological analysis. In the laboratory, two sub cores were extruded and sliced inside a  $\text{N}_2$  filled glove bag at 1 cm intervals down to 10 cm and at 2 cm intervals below 10 cm. A total of 17 samples from Core 8 (21 cm long) and 16 from Core 16 (22 cm long) were collected. The sediment samples were dried ( $T = 35\text{ }^{\circ}\text{C}$ ) and homogenised before the mineralogy phases, Total Organic Carbon (TOC) and THg were determined. An SSE procedure was carried out on sediment from two sub cores. In Particular, 3 cm slices for a total of nine samples were analyzed.

### 2.3. Geochemical analyses

#### 2.3.1. Sediment

The mineralogy of the bulk samples was investigated by X-ray diffraction (XRD), using a D8 Discover Bruker equipped with a Sol-X detector. The instrumental conditions were Cu-K $\alpha$  radiation and a scanning speed of  $2.2\text{ }^{\circ}/\text{min}$ . The semi-quantitative analysis of the minerals

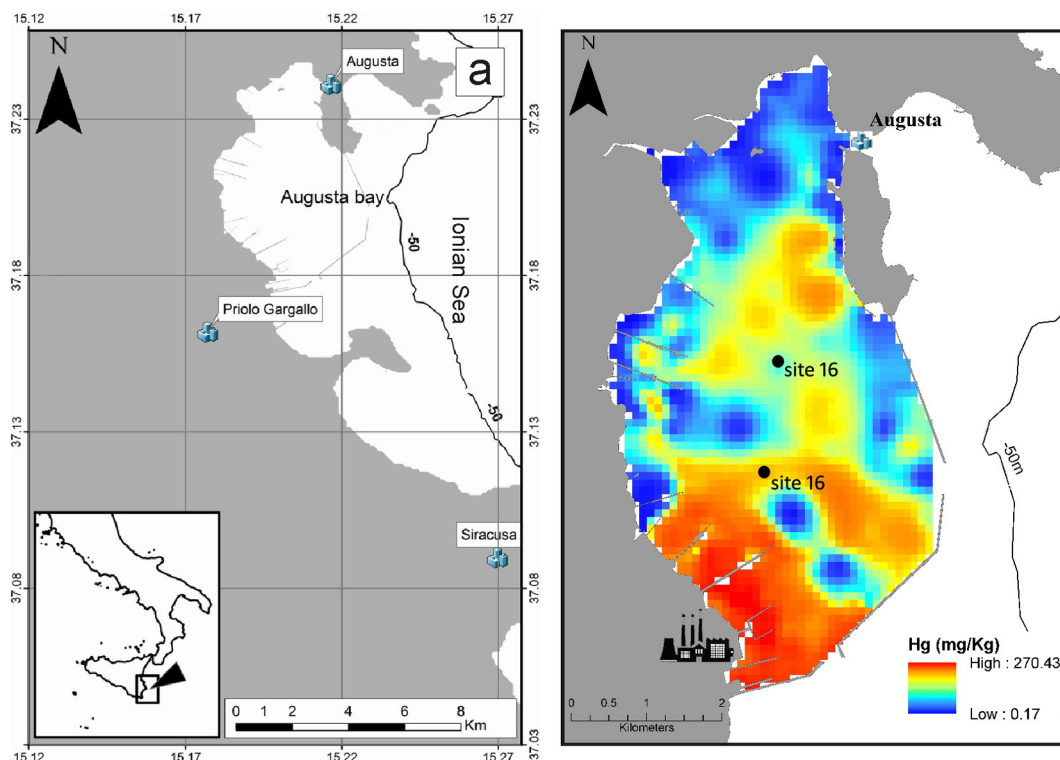


Fig. 1. a) Location map of the Augusta Bay; b) distribution map of total mercury (THg) in bottom sediments with sampling sites in the Augusta harbour.

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