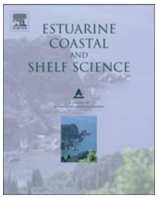
Estuarine, Coastal and Shelf Science 93 (2011) 7–13

Contents lists available at ScienceDirect

Estuarine, Coastal and Shelf Science

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



Relocation effects of dredged marine sediments on mercury geochemistry: Venice lagoon, Italy

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ARTICLE INFO

Article history:
Received 28 January 2010
Accepted 7 March 2011
Available online 17 March 2011

Keywords:
mercury
pore water
sediment pollution
vertical profiles
Venice Lagoon

ABSTRACT

Understanding the biogeochemical process of Hg is critical in the overall evaluation of the ecological impacts resulting from the reuse of Hg-contaminated dredged sediment. Sediment banks (V1 and V2) were constructed with freshly dredged sediments from a navigational channel in Venice Lagoon, Italy, with the goal of clarifying potential differences in the biogeochemistry of Hg between the reused dredged sediments and those from surrounding sites (SS1 and S2). Toward this purpose, Hg and monomethylmercury (MMHg) concentrations, and Hg methylation rates (MMRs) in the surface 2.5 cm sediments were monitored, along with ammonium, iron, sulfate and sulfide concentrations in the pore waters of banks and surrounding sites from November 2005 to February 2007. Pore water analyses indicate that the bank sediments are characterized by lower levels of sulfate and iron, and by higher levels of ammonium and sulfide compared to the surrounding sediments. With respect to Hg speciation, the fractions of MMHg in total Hg (%MMHg/Hg) and the MMRs were significantly lower in the bank V1 compared to those in the reference site SS1, whereas the %MMHg/Hg and the MMRs were similar between V2 and S2. A negative correlation is found between the logarithm of the particle-water partition coefficient of Hg and the MMR, indicating that the reduced MMRs in V1 are caused by the limited concentrations of dissolved Hg. Organic matter appears to play a key role in the control of MMR via the control of Hg solubility.

1. Introduction

Dredging and the disposal of dredged materials are important issues concerning coastal area management. Surface sediment is dredged from estuaries and coastal areas to maintain navigation channels and often to remove contaminated materials (Alden and Young, 1982; Levinton et al., 2006). Major concerns have arisen over where to dispose of this dredged material and the ecological impacts of such disposals (Levinton et al., 2006; Burchell et al., 2007). In recent years, dredged materials have been relocated for environmentally beneficial purposes, such as the rejuvenation of intertidal habitats (Burchell et al., 2007). However, this type of relocation has been practiced only on a small scale due to a lack of understanding regarding the ecological impacts that follow the reuse of dredged sediment. Understanding the biogeochemical processes involving these contaminants is critical in the overall evaluation of the ecological impacts resulting from the reuse of dredged sediment.

To understand the biogeochemical processes of contaminants involved in the reuse of dredged channel sediment in the Venice Lagoon, Italy, the SIOSED (Scripps Institution of Oceanography SEDiment research) program was conducted from March 2005 to November 2007 (Deheyn and Shaffer, 2007). Sediments were dredged from a navigation channel and transplanted onto two shallow sites. At the relocated and surrounding (reference) sites, a multidisciplinary study was carried out, including studies on the geochemistry of trace metals, microbial community, fauna and flora content, and sedimentary ecotoxicology. This type of monitoring program was essential because the sediment in the Venice Lagoon is contaminated with various metals and organic pollutants, and consequently, most of the sediment in the lagoon has been evaluated as potentially hazardous (Frignani et al., 1997; MAV-CVN, 2004).

Mercury is one of the most serious pollutants in the Venice Lagoon (Bloom et al., 2004; Han et al., 2007a), posing a potential

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doi:10.1016/j.ecss.2011.03.004

threat to public health and marine ecosystems. Most Hg contamination in the Venice Lagoon originates from past occurrences between the 1950s and 1980s, especially from the chlor-alkali discharge located in the petrochemical zone of Porto Marghera (Bloom et al., 2004). Thus, Hg concentrations in the subsurface sediment are often higher than those in the surface sediment (Bloom et al., 2004; Han et al., 2007a). Considering the mass balance calculations using various physical volumes and flows, it has been demonstrated that Hg flux to Venice Lagoon water is dominated mainly by the resuspension of contaminated sediment (Bloom et al., 2004). The current pollution input from rivers, industry, and precipitation has been estimated to be less than 25% of the total Hg flux, highlighting the importance of the resuspension flux (Bloom et al., 2004).

We speculated that the reuse of dredged sediment from the navigation channel may increase the concentration of the more toxic form of Hg, monomethylmercury (MMHg), compared to those found in the reference sediment by several reasons. First, the dredged sediment from the navigation channel may contain higher concentrations of MMHg than in the reference sediment because of common characteristics of channel sediments, such as enhanced organic concentrations and microbial activities. Secondly, the solubility of Hg in the dredge sediment would be higher than that in the reference sediment, perhaps due to the oxidation of iron sulfide and consequent release of dissolved Hg (Hammerschmidt and Fitzgerald, 2004; Rothenberg et al., 2008) when Hg-contaminated subsurface sediment is exposed to the surface and air during the dredging activity. This process would lead to higher Hg methylation rates (MMRs), if the dissolved Hg is a limiting factor for the net MMR, as evidenced in several estuarine and coastal sediments (Hammerschmidt and Fitzgerald, 2004; Wolfenden et al., 2005; Hammerschmidt et al., 2008). Finally, a reduction in the dissolved sulfide concentration in pore waters of the dredge sediments, due to the potential destruction of anoxic conditions during the dredging activities, may produce favorable conditions for Hg-methylating organisms to uptake inorganic Hg via increasing neutral Hg-sulfide species (Benoit et al., 1999; Drott et al., 2007; Han et al., 2007b, 2008). Based on these assumptions, experimental banks were built with freshly dredged sediments from a navigational channel in the Venice Lagoon, and Hg speciation and pore water geochemistry were monitored over a period of 18 months. In the present study, we report the Hg and MMHg concentrations, and Hg methylation rates in bank and reference sediments along with dissolved Hg, Fe, ammonium, sulfide, and sulfate concentrations in pore waters.

2. Material and methods

2.1. Study area

The study area consisted of three sites (Fig. 1): SS0, SS1, and S2. Freshly dredged sediment from approximately the top 1 m layer of site SS0, a previously dredged channel, was transplanted into SS1 and S2 (1.4 m water depth) to create subtidal dredge sediment banks, bank V1 in site SS1 and bank V2 in site S2, between October 25, 2005, and November 16, 2005. The sediment was dredged from SS0 using an excavating crane equipped with a clamshell grab on a barge; the sediment ($\sim$220 m^3) was re-excavated from the barge and redeposited into the delimited areas that had been designated for making the banks. Initially, the relocated sediment was contained by wood pilings to protect against immediate erosion. The wood pilings were removed in June 2006 after the bank sediment had compacted and stabilized. The heights of both banks (V1 and V2) were reduced from 1 m to 70 cm following the natural compaction and stabilization of the sediment, which was below sea level even at low tide. The width and length of the banks were 30 m and 10 m, respectively (Deheyn and Shaffer, 2007). The surface sediment in SS1 was more sandy and contained less organic carbon than that in S2, and the dredged sediment from SS0 contained more organic carbon than the reference sediments (Table 1).

2.2. Sample collection

Sampling of the sediment commenced shortly after the bank construction. Surface (2.5 cm) sediment was collected using short push cores in November 2005, and February, June, and July 2006, and February 2007. Long piston cores or vibracores (1.5 m or 30 cm) were collected in December 2005, and in May, September, and November 2006. The collected cores were extruded and sectioned (0–2.5, 2.5–5, 5–7.5, 7.5–10, 10–15, and 15–20-cm intervals) within 24 h in a N_2-filled glove box in the laboratory of Thetis SpA (Venice, Italy), thus preventing the oxidation of sulfide and dissolved ferrous iron.

After the extrusion and sectioning of cores in the glove box, pore waters were extracted by centrifuging under nitrogen conditions at approximately 5000 rpm. After filtering the pore water samples using 0.45-mm pore size polyethersulfone syringe filters under anaerobic conditions, approximately 10–20 cm^3 of the filtered pore water sample was acidified for the analysis of dissolved Hg and Fe, and the remainder was used for measurements of dissolved sulfate, sulfide, and ammonium. The remaining sediment slices were stored frozen for analyses of sedimentary Hg and MMHg. Separately, approximately 20 g of the sediment slices were sealed in amber glass vials under N_2 saturated conditions and transported to the SIO laboratory in a portable electric cooler (4 °C) for Hg methylation experiments. Hg methylation experiments were carried out within 1 week after sampling.

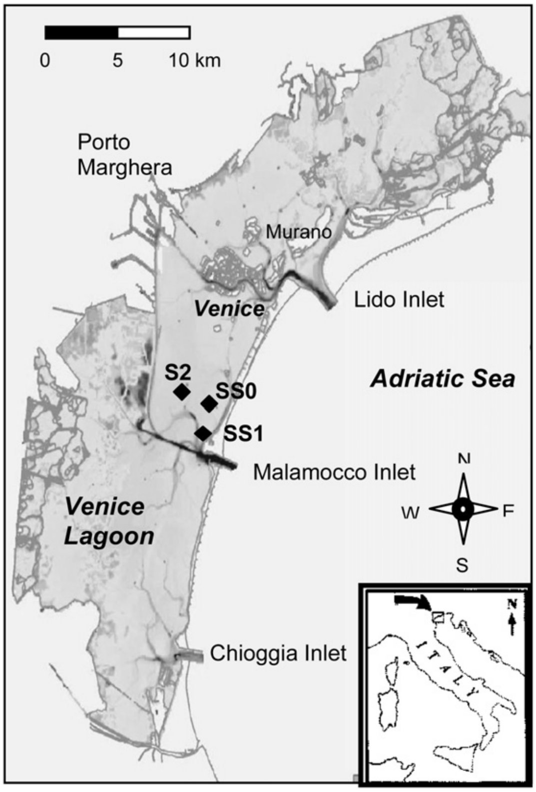

Fig. 1. Locations of sediment banks (V1 bank in SS1 and V2 bank in S2) and the dredged channel site (SS0) in the Venice lagoon, Italy.