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Anthropogenic contaminants in Venice Lagoon sediments and their pore fluids: Results from the SIOSED Project

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ABSTRACT

Investigations of sediment geochemistry and interstitial water chemistry during SIOSED (Scripps Institution of Oceanography Sediment Research Project) revealed information about the characteristics and depth range of contamination in sediments associated with dredging operations in the Venice Lagoon, Italy. Results from gravity cores indicate that contamination ranges larger and deeper in sediments associated with Porto Marghera and the Venice Industrial Zone compared with sediments at greater distances from dredged shipping canals or pollution sources. The effects of sediment re-deposition were evaluated from a pore water chemistry study of artificial banks constructed by placing dredged canal sediments on top of background sediments. Rapid decreases in dissolved sulfate associated with increases in alkalinity, sulfide, and nutrients, such as ammonium and phosphate, indicate that sediment dredging led to enhanced bio-chemical diagenesis of organic matter near the surface of the re-deposited sediments. Continued diagenesis of organic matter in re-deposited sediments maintained extrema in alkalinity, dissolved sulfate, sulfide, and ammonium. The artificial banks retained their pore water signatures over the duration of the project. Sediment redistribution can thus cause important changes in pore water profiles, as observed from the chemistry in long cores studied in this program.

1. Introduction

Sediments of the Venice Lagoon, Italy are influenced by a number of dynamic physical and geochemical processes that are affected by both natural and anthropogenic activities. The distribution of trace metal contaminants temporarily sequestered in Venice Lagoon sediments and interstitial waters are of particular concern for those managing fishing, industrial and recreational activities, and ecosystem health. As a consequence, the mapping of seafloor contaminants and their concentrations has been a primary focus of geochemical work in the Lagoon. Studies by Donazzolo et al. (1984), Frignani et al. (1997), and Bellucci et al. (2002, 2005) established the principal areas of contamination near Porto Marghera and the Industrial Zone of Venice, with enrichments of some trace metals (e.g., copper and zinc) also evident in less contaminated areas of the Lagoon (Pavoni et al., 1987; Lucchini et al., 2001–2002). Maps of the distribution of metals were presented in reports to the Consorzio Venezia Nuova (Magistrato alle acque di Venezia, 2004a,b), summarizing much of this information.

The history of anthropogenic influences on the Lagoon is evident in seafloor sediment characteristics. Trace metal inputs to the Lagoon increased dramatically in the early 1930s with the development of industry in the Porto Marghera area (Frignani et al., 1997; Cochran et al., 1998; Bellucci et al., 2002, 2005). Increases in trace metal contamination at that time were reported both in the North-Central and the South-Central Venice Lagoon, providing an effective time marker for sediment studies. Changes in sediment deposition and sedimentation rates affected the sediments of the central part of the Lagoon during the late 1990-ies (Sfriso et al., 2005; Bernardelo et al., 2006). These changes were mostly due to sediment suspension and removal during intensive clamming operations in recent years. A reduction of the macro-algal beds before and after the initiation of clam fishing by means of highly disruptive techniques has significantly contributed to the increase (~ one order of magnitude) of fine sediment fraction re-suspension and spreading, favoring a loss of fine material and a homogenization of the surface

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sediments with consequent changes in the surface distribution of trace metals (Sfriso et al., 2005; Bernardelo et al., 2006). Special attention has also been given to the distribution of mercury in its various forms, both in the waters and the sediments of the Lagoon (Bloom et al., 2004a, 2004b; Han et al., 2007, 2010). For mercury there also are higher concentrations in the vicinity of Porto Marghera and around the southern end of the city of Venice (Magistrato alle acque di Venezia, 2005; Han et al., 2010; Molinaroli et al., 2013).

Especially in the area of Porto Marghera contamination of the sediments has been large. Molinaroli et al. (2013) present comparisons of mercury and zinc contents in these sediments between the years 1970 and 2008 in the vicinity of Porto Marghera. These authors showed by means of mass balance calculations, that as a result of reduced contamination as well as redistribution and exportation of the sediments into other areas of the lagoon and into the Adriatic Sea, surface sediments in the Porto Marghera area indicate diminished contamination.

Redistribution of Venice Lagoon sediments remains an important activity in part to keep shipping lanes open to large sea-going vessels. In addition currents and fishing operations also have caused redeposition of sediments. Relationships between redistributed sediments, surface sediment characteristics, and down-core sediment and pore water geochemistry in the Venice Lagoon play a strong role in the distribution of contaminants. Examination of sediments and pore waters from recently disturbed seafloor locations can provide important clues about the geochemical consequences of sediment redistribution in the Lagoon (Magistrato alle acque di Venezia, 2005). Geochemical analyses reveal appreciable geographic variability throughout the Lagoon (*Appendix: Supplemental Information—section 1*). In comparable studies, gradual decreases in contaminant concentrations are commonly evident in areas where inputs of the pollutants have been diminished through regulation. For example, Santschi et al. (2001) noted that trace metal profiles off the Palos Verdes (California) indicated a decrease in contaminants with changes in sewage output from Los Angeles. Similarly, with a gradual diminishing of pollutant inputs from Porto Marghera, decreases in trace metal inputs into the sediments in Venice Lagoon are likely.

Near-surface sediments have been the focus of much of the previous work on Venice Lagoon pore fluids, including the distribution and fluxes of trace metals and nutrients in the interstitial fluids of the upper 10–20 cm of the sediment column (e.g., Scholten et al., 2000; Magistrato alle acque di Venezia, 2003, 2004b). Available data for the year 2001 indicated that interstitial water dissolved copper concentration levels in the vicinity of Porto Marghera (Station 9B of Magistrato alle acque di Venezia, 2003) were generally below 160 nM, and concentrations of zinc were below 280 nM (c.f., Figs. 3.6–7 of Magistrato alle acque di Venezia, 2003). Reported copper concentrations in overlying waters were < 160 nM and Zn concentrations were < 325 nM in the central north and central parts of the Venice lagoon. On the other hand, Turetta et al. (2005) reported overlying water Cu of < 20 nM and Zn < 90 nM, with much higher concentrations at the sediment water interface in the Porto Marghera area. Lagoonal averages of dissolved Zn from 2001 to 2003 reported by Thetis ranged from 27 nM in the areas away from the sources of contamination to 160 nM in the Porto Marghera area (*Appendix: Supplemental Information—section 1*). For the same time interval dissolved Cu ranged from 25 to 65 nM (Magistrato alle acque di Venezia, 2004c, 2005). Much of the Cu and Zn in the overlying waters may be associated with organic ligands (e.g., Rivera-Duarte et al., 2005). Delgadillo-Hinojosa et al. (2008) report total Cu concentrations in the Porto-Marghera area of 20–70 nM, again mostly in the area of Porto Marghera and the Industrial zone. The latter authors found that most of the copper is bound to organic compounds.

In this paper we present results of investigations of sediment geochemistry and associated chemistry of the interstitial waters recovered in the Venice Lagoon under the auspices of the Scripps Institution of Oceanography Sediment Research Project (SIOSED). SIOSED investigations were designed to study the effects of sediment relocation on the geochemistry, biology, bacteriology, and benthic foraminiferal chemistry of the sediments (Deheyn and Shaffer, 2007). Towards these ends a background program of sediment coring was carried out with the purpose of studying the geochemistry of the solid phases, and their connate interstitial waters (cf, Gieskes et al., 2011a,b). Many of these sampling sites were associated with dredged canals, either from the canals themselves or in a zone of dredge material deposition (Sites C, SO, SSO in Fig. 1).

As part of the SIOSED program the distribution of salinity in the waters in the central south Lagoon, as well as of dissolved chloride in the sedimentary pore fluids has been described in more detail by Gieskes et al. (2013). In addition, Zirino et al. (2014) discussed the distribution of salinity in the entire Venice Lagoon and its variability.

2. Site descriptions

The locations chosen for this study (Fig. 1) consisted of a number of sites throughout the Venice Lagoon that were relevant to the SIOSED program. Site descriptions are summarized in Table 1. Seafloor sediments of the Venice Lagoon have been placed into categories (A, B, or C) based on the individual concentrations of a group of selected trace metals (Magistrato alle acque di Venezia, 2004a,b; Gieskes et al., 2011a). Sediments of class A have lower concentrations of these trace metal contaminants, while Class C sediments have a high concentration of at least one of the target contaminants, generating considerable concern (Magistrato alle acque di Venezia, 2004a,b; Apitz et al., 2007) (*Appendix: Supplemental Information—section 1*; Gieskes et al., 2011a).

Site SO is located near the Industrial Zone southwest of Venice and is associated with a well used ship canal in the area of San Angelo delle Polveri. Site SO consists of Class B sediments, whereas Site S1 is a reference site for Site SO located in Class A sediments.

Site SSO is located in the Canale Campana near the Malamocco Inlet. Sediments of SSO consist of Class A/B sediments, and have served as a source for sediments to be put on top of sediments of Sites SS1 and S2, thus creating artificial banks of approximately 70–90 cm above their respective reference sediments (Deheyn and Shaffer, 2007). These locations are then summarized as Sites V1 and V2. The sediment banks have been the major subjects of research by the SIOSED program.

Site A was located near San Erasmo in the Northern part of the Lagoon and consisted mostly of sandy sediments. Site B was located in the Paludo Maggiore in the North Eastern part of the Venice Lagoon and has been described as a Class B sediment.

Site C was located in the vicinity of "I Pili" in the contaminated zone (Class C sediments) near Porto Marghera, where intensive clean-up operations have been almost completed in the year 2009. As a result of extensive dredging in this area, sediments were not expected to be homogeneous in nature.

Drill hole SM3 reached the interface between Lagoon sediments and deeper sedimentary strata below ~11 m depth. In the deeper strata evidence for underlying aquifers is apparent from the much lower chlorides at these depth horizons (Gieskes et al., 2011b, 2013).

3. Methods

Sediments were obtained from gravity cores of ~125 cm length (long cores) and push cores of ~25 cm length (short cores), as well as from one drill hole (SM3) in the Porto Marghera area of Venice lagoon. The locations of the sampling sites are indicated in Fig. 1.

We report data obtained for the solids through three different means:

(1) Whole core scanning of gravity cores with X-Ray fluorescence (*Appendix: Supplemental Information—section 2* and Gieskes et al., 2011a);