



Porewater dynamics of silver, lead and copper in coastal sediments and implications for benthic metal fluxes



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HIGHLIGHTS

- Porewater profiles of silver, copper and lead for two coastal sites are presented.
- High trace metal fluxes only occur in winter at sulfidic sites.
- The Cu diffusive flux contributes to the elevated metals in Boston Harbor waters.
- Trace metal enrichment can develop at the surface of sites with no sulfide.
- Metal contamination will persist at the surface due to this enriched layer.

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ABSTRACT

To determine the conditions that lead to a diffusive release of dissolved metals from coastal sediments, porewater profiles of Ag, Cu, and Pb have been collected over seven years at two contrasting coastal sites in Massachusetts, USA. The Hingham Bay (HB) site is a contaminated location in Boston Harbor, while the Massachusetts Bay (MB) site is 11 km offshore and less impacted. At both sites, the biogeochemical cycles include scavenging by Fe-oxyhydroxides and release of dissolved metals when Fe-oxyhydroxides are reduced. Important differences in the metal cycles at the two sites, however, result from different redox conditions. Porewater sulfide and seasonal variation in redox zone depth is observed at HB, but not at MB. In summer, as the conditions become more reducing at HB, trace metals are precipitated as sulfides and are no longer associated with Fe-oxyhydroxides. Sulfide precipitation close to the sediment–water interface limits the trace metal flux in summer and autumn at HB, while in winter, oxidation of the sulfide phases drives high benthic fluxes of Cu and Ag, as oxic conditions return. The annual diffusive flux of Cu at HB is found to be significant and contributes to the higher than expected water column Cu concentrations observed in Boston Harbor. At MB, due to the lower sulfide concentrations, the association of trace metals with Fe-oxyhydroxides occurs throughout the year, leading to more stable fluxes. A surface enrichment of solid phase trace metals was found at MB and is attributed to the persistent scavenging by Fe-oxyhydroxides. This process is important, particularly at sites that are less reducing, because it maintains elevated metal concentrations at the surface despite the effects of bioturbation and sediment accumulation, and because it may increase the persistence of metal contamination in surface sediments.

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1. Introduction

The sediments of the coastal zone have been a sink for contaminants discharged to the environment for centuries. With improved environmental legislation, the direct discharge of pollutants has been significantly reduced in recent decades (Bothner et al., 1998; Luoma and Rainbow, 2008; Birch et al., 2013). Nevertheless, the legacy of contaminated sediments remains. Sediments have been shown to supply

dissolved trace metals to the water column in quantities greater than riverine fluxes in many regions: Pb and Ag in San Francisco Bay, USA (Rivera-Duarte and Flegal, 1994, 1997a); Cu and Pb in the north-eastern Irish Sea (Williams et al., 1998); and Cu, Ni and V in the Vigo Ria, Spain (Santos-Echeandia et al., 2009). Despite the potentially important impact on coastal water quality, the mechanisms that determine if a metal is permanently sequestered in the sediment or remobilized to the water column is not well established.

Trace metal behavior is controlled by the early diagenetic reactions within the sediments. Only dissolved metals can be released from stable (not eroding) sediment. The dissolved metals can be transported to the

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overlying water by diffusion, flushing by benthic organisms irrigating their burrows (Burdige, 2006) or advective flow in permeable sediments driven by waves, tides, and pressure gradients from microtopography (Huetzel and Webster, 2001). Reactions that increase the dissolved metal concentration by converting solid-phase trace metals to the porewater phase can increase the metal release to the overlying water. In coastal sediments, these reactions are coupled to the oxidation of organic carbon, especially when Fe and Mn-oxyhydroxides and sulfate are the terminal electron acceptors. Specifically, mineralization of organic carbon can supply metals to porewaters (Heggie et al., 1986; Shaw et al., 1990; Audry et al., 2006), whereas trace metals are scavenged and removed from porewaters by Fe and Mn-oxyhydroxides (Burdige, 1993; Sundby, 2006). The reductive dissolution of these carrier phases can in turn release trace metals to porewaters (Shaw et al., 1990; Canavan et al., 2007). Sulfide, formed during sulfate reduction, precipitates insoluble trace metal phases (Rosenthal et al., 1995; Gobeil et al., 1997; Morse and Rickard, 2004), and the oxidation of sulfides can release dissolved metals. The relative importance of these opposing processes is unknown and it is difficult to predict the net effect of these reactions on trace metal cycling (Sundby, 2006).

In the coastal zone, trace metal cycles are particularly challenging to predict due to continually varying conditions. The sediments are subject to strong seasonal variations in organic and terrigenous matter flux, water column stratification, temperature and benthic macroinvertebrate activity. The early diagenetic processes and redox zones within the sediments vary considerably over the course of a year, and so do the reactions competing for trace metals. Despite the variability in processes that impact metal mobilization, seasonal changes in porewater concentrations and benthic metal fluxes have been investigated in only a limited number of locations worldwide (Hines et al., 1984; Westerlund et al., 1986; Warnken et al., 2001; Gao et al., 2009; Lourino-Cabana et al., 2014). The stability of the seasonal variation in these studies is unknown, due to limited periods of observation, and the dominant controls on metal release and burial remain elusive.

Here we present a record of trace metal porewater concentrations collected over seven years from contaminated sediments in Boston Harbor, USA, with the objectives of (1) quantifying the diffusive flux from sediments in different seasons; (2) establishing how consistent the seasonal fluxes are between years; and (3) determining the diagenetic reactions which influence the magnitude of the diffusive flux and the ultimate burial of trace metals. We show stable seasonal cycles in metal remobilization and benthic flux that are consistent between years, even as the sediment conditions evolve due to reduced contaminant discharge. The cycle identified in Boston Harbor is contrasted with seasonal porewater profiles from a less impacted offshore site in nearby Massachusetts Bay to assess the general applicability of the cycle. The important contaminant metals Ag, Pb, and Cu are investigated. All previously published coastal Ag porewater profiles are from San Francisco Bay (Rivera-Duarte and Flegal, 1997a; Huerta-Diaz et al., 2007). The data presented here extend Ag results to additional locations, providing new information on the distribution of an element that remains poorly understood in marine environments (Tappin et al., 2010). This long term record of trace metals in porewaters provides new insight into the fate of metals in contaminated coastal sediments. Our findings suggest longer persistence of metal contamination in the surface sediments of less reducing sites, due to diagenetic processes that maintain the metals at the surface, despite the effects of bioturbation and sediment accumulation.

2. Study sites

Boston Harbor is an urban estuary in coastal Massachusetts USA, partially surrounded by the city of Boston (Fig. 1). The sediment and water quality of the Harbor have been degraded by more than 130 years of sewage discharge. In the 1980s the nutrient loads to the Harbor were among some of the highest in the world (Kelly, 1997),

and based on metal and persistent organic pollutant concentrations in the sediment, it was considered the most contaminated harbor in the United States (Bothner et al., 1998). A comprehensive modernization of greater Boston's wastewater treatment facilities was initiated in the 1980s to address the deteriorating sediment and water quality of the Harbor. The upgrade proceeded in stages, with sewage sludge discharge to the Harbor ending in 1991 and effluent discharge from the Nut Island wastewater treatment plant (Fig. 1) ending in 1998. In 2000, secondary treatment of sewage was implemented and discharge of treated sewage effluent was diverted from the harbor mouth to the Massachusetts Bay outfall, 15 km offshore (Taylor et al., 2011) (Fig. 1). Due to the reductions in sewage discharge, as well as improvements in chemical techniques to recover metals from industrial wastes, and the phaseout of leaded gasoline, the concentrations of metals in the sediments of Boston Harbor have decreased (Bothner et al., 1998; Zago et al., 2001). The concentration of metals in the water column of the Harbor however, did not decrease significantly between 1991 and 2002. A combined hydrodynamic-water quality model of the Harbor predicted dissolved concentrations of Pb and Cu that were less than 20% of measured values, which is likely due to benthic fluxes from contaminated sediments (Li et al., 2010). We conducted the study described here to determine the mechanisms that drive the benthic metal flux.

Two fine-grained sediment sites (Table 1) with contrasting contamination histories were investigated (Fig. 1). Both are located in depositional areas of the Bay (Knebel et al., 1991), where the bottom water oxygen concentration is close to saturation throughout the year, with maximum oxygen concentrations in February (380 μM) and minimum in October (250 μM). The Hingham Bay site (HB) in Boston Harbor is shallow (5 m water depth) with 94% fine-grained sediment. The average proportion of fines in the surface sediment did not change between 2002 and 2008 (at the 95% level of certainty). There are historically high trace metal concentrations due to past sewage discharge from the nearby Nut Island wastewater treatment plant (Bothner et al., 1998). The average organic carbon contents in the surface sediment over 2002–2004 were $3.0 \pm 0.2\%$, and $2.6 \pm 0.1\%$ in 2008 (average \pm standard deviation, Table 1). The 2008 average value is statistically different from the earlier value (95% level of certainty), consistent with the observations of Tucker et al. (2014) that the surface organic carbon content has decreased over time due to the reductions in sewage discharge. Morford et al. (2007) determined that the average organic carbon oxidation rate at HB in 2001–2002 was $880 \mu\text{mol C/cm}^2/\text{yr}$, the oxygen penetration depth was less than 4 mm, bioirrigation was active at the site with a maximum in early summer, and bioturbation was seasonal, with a bioturbation coefficient of $3 \text{ cm}^2/\text{yr}$ in winter and $20\text{--}25 \text{ cm}^2/\text{yr}$ in June and October. The most abundant organism was the tube-building amphipod *Ampelisca* spp. with *Leptocheirus pinguis* also important in 2008 (Tucker et al., 2014). There were $0.3\text{--}1 \times 10^5$ organisms/ m^2 retained on a 1 mm sieve in the spring and summer of 2003 (Benoit et al., 2006). Measurements of burrow surface area show burrows present to a maximum depth of 6 cm (Benoit et al., 2006) and the depth of bioturbation is also unlikely to extend below 6–8 cm, the depth where dissolved sulfide is detected in the porewaters (Morford et al., 2009). The sedimentation rate was 1.8 cm/yr in 1978 (Bothner et al., 1998) and has since declined considerably due to cessation of sewage discharge. The annual average sedimentation rate between 1978 and 2000 (estimated from ^{137}Cs profiles) was 0.6 cm/yr (Morford et al., 2007), which is likely biased by high sedimentation rates before 1991 when sewage sludge was still discharged to the Bay, so the sedimentation rate after 2000 is even lower.

The second study site is 11 km offshore in Massachusetts Bay. This site (MB) is in 30 m of water and is 2 km west of the nearest diffuser port in the offshore sewage outfall (Fig. 1). There is 82% fine-grained sediment, 2% organic carbon and the average rate of organic carbon oxidation ($600 \mu\text{mol C/cm}^2/\text{yr}$ (Martin and Kalnejais, 2007)) is about two-thirds that at HB. The oxygen penetration depth is less than 6 mm (Sayles and Goudreau, 2007). Bioturbation at MB is complex and not well described by biodiffusive mixing models (Crusius et al., 2004).

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