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ScienceDirect
Chemosphere 69 (2007) 1428–1437
CHEMOSPHERE
www.elsevier.com/locate/chemosphere

Effect of overlying water pH, dissolved oxygen, salinity and sediment disturbances on metal release and sequestration from metal contaminated marine sediments

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Received 21 December 2006; received in revised form 23 April 2007; accepted 25 April 2007
Available online 12 June 2007

Abstract

Experiments were undertaken to examine the key variables affecting metal release and sequestration processes in marine sediments with metal concentrations in sediments reaching up to 86, 240, 700, and 3000 mg kg^{-1} (dry weight) for Cd, Cu, Pb and Zn, respectively. The metal release and sequestration rates were affected to a much greater extent by changes in overlying water pH (5.5–8.0) and sediment disturbance (by physical mixing) than by changes in dissolved oxygen concentration (3–8 mg l^{-1}) or salinity (15–45 practical salinity units). The physical disturbance of sediments was also found to release metals more rapidly than biological disturbance (bioturbation). The rate of oxidative precipitation of released iron and manganese increased as pH decreased and appeared to greatly influence the sequestration rate of released lead and zinc. Released metals were sequestered less rapidly in waters with lower dissolved oxygen concentrations. Sediments bioturbated by the benthic bivalve *Tellina deltoidalis* caused metal release from the pore waters and higher concentrations of iron and manganese in overlying waters than non-bioturbated sediments. During 21-day sediment exposures? *T. deltoidalis* accumulated significantly higher tissue concentrations of cadmium, lead and zinc from the metal contaminated sediments compared to controls. This study suggests that despite the fact that lead and zinc were most likely bound as sulfide phases in deeper sediments, the metals maintain their bioavailability because of the continued cycling between pore waters and surface sediments due to physical mixing and bioturbation.

Keywords: Metal release and sequestration; Contaminated sediments; Bioturbation and physical disturbance; Sediment-metal bioavailability; Physico-chemical parameters

1. Introduction

In most aquatic environments, dissolved metal concentrations in overlying waters are low due to precipitation as solids or adsorption to suspended particles and the deposition of these particles as sediments. Once deposited as sediments, biological and chemical oxidation/reduction and precipitation/dissolution reactions result in the redox stratification of both dissolved and particulate metals with sediment depth. The oxic fraction of silty sediments usually extends to depths of 2–5 mm (Kristensen, 2000). At greater depths the sediment becomes sub-oxic, containing mixtures of oxic solid phases (e.g. Fe- and Mn-(hydr)oxides) in equilibrium with reduced dissolved phases (e.g. Fe(II) and Mn(II)) (Simpson and Batley, 2003). Once the easily reducible Fe- and Mn-(hydr)oxide phases have been depleted, bacteria reduce sulfate to sulfide, which reacts to form metal sulfide complexes whose solubility controls the fraction of metals dissolved in solution (Di Toro et al., 1992; Burdige, 1993).

The fate and toxicity of metals in the sediments is greatly dependent on the partitioning of metals between the

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doi:10.1016/j.chemosphere.2007.04.068

sediment particles and the pore waters (Calmano et al., 1993; Simpson, 2005). Dissolved metals present in the pore waters are more bioavailable and toxic than particulate metals (Chapman et al., 1998). Physical processes (e.g. water currents, anthropogenic disturbance) and the activity of benthic organisms (e.g. burrowing, irrigation) can cause sediment resuspension and mixing of previously redox-stratified sediments with oxygenated overlying waters. This resuspension and mixing alters metal sediment–water partitioning and metal speciation in the dissolved phase, i.e., pore waters and overlying waters (Riedel et al., 1997; Kristensen, 2000; Simpson et al., 2002). These physico-chemical changes alter the bioavailability of metals in the pore waters (Ciutat and Boudou, 2003; Simpson and Batley, 2003) and the release rate (flux) of metals from the sediments (Simpson et al., 2002). The fate (speciation) of metals released from sediments is affected by overlying water conditions, in particular the pH, salinity, dissolved oxygen concentration and amount of suspended solids (Eggleton and Thomas, 2004; Simpson et al., 2004). Understanding the key factors that influence the release of metals from sediments would allow better prediction of the changes in metal availability to sediment-dwelling organisms.

This research investigated the influence of the overlying water parameters pH, dissolved oxygen (DO) concentration and salinity on metal release from metal contaminated estuarine sediments in shallow waters. One at a time, each of the three test parameters was selected and varied to low, mid and high values of the parameter, whilst maintaining the other parameters at near constant values. The release of metals across the sediment–water interface into the overlying water, and subsequent sequestration of these released metals was studied with each parameter over a 21-day period. These experiments were performed on bioturbated and non-bioturbated sediments, using the sediment ingesting bivalve *Tellina deltoidalis*. After 21 days the animals were recovered from the test sediments and analysed for metal accumulation in comparison to organisms exposed to a control uncontaminated sediment to ascertain the bioavailability of the sediment-metals. Further, in an attempt to understand the effects of the overlying water parameters in the event of a significant sediment disturbance, the contaminated sediment that had been observed for 21 days were physically mixed and metal release to and sequestration from the overlying water were investigated for up to 9 days.

2. Materials and methods

2.1. Study site and sampling

Metal contaminated sediments were collected from the Pb–Zn smelter contaminated Cockle Bay in Lake Macquarie, New South Wales, Australia (151°30′E, 33°00′S). Surface (0–5 cm) and depth (10–15 cm) sediment cores were collected from 13 sites (Fig. 1) within 3–10 m of the shoreline using a polycarbonate corer (5 cm diameter × 30 cm) to identify the optimal sediment for this study. Bulk sediment samples for metal release and bioavailability experiments (30 kg, 0–15 cm depth) were collected, using a shovel from Site 6 (Fig. 1), and sieved on-site through 1 mm mesh to remove large debris. Control bulk sediments, used in the metal bioavailability study, were collected in the same manner from Boronia Park, an uncontaminated bay of the estuarine Lane Cove River, Sydney (Table 1). All sediments were stored in the dark at 4 °C and used within one week of collection. The sieved sediments contained some small benthic organisms (predominantly amphipods at five organisms per 100 g sediment) but were considered non-bioturbated in comparison to the grossly disturbed sediments that were physically mixed or contained bivalves. Clean seawater (salinity of 35–45 PSU) was collected from Fairy Meadow, NSW, Australia.

The sediment ingesting bivalves, *T. deltoidalis*, were collected from estuarine sand and mud flats of Lane Cove River, according to the method of King et al. (2004). Approximately 400 bivalves (15–35 mm shell length) were collected for bivalve bioturbation tests and 50 bivalves (16 ± 1 mm shell length) for metal bioavailability experiments.

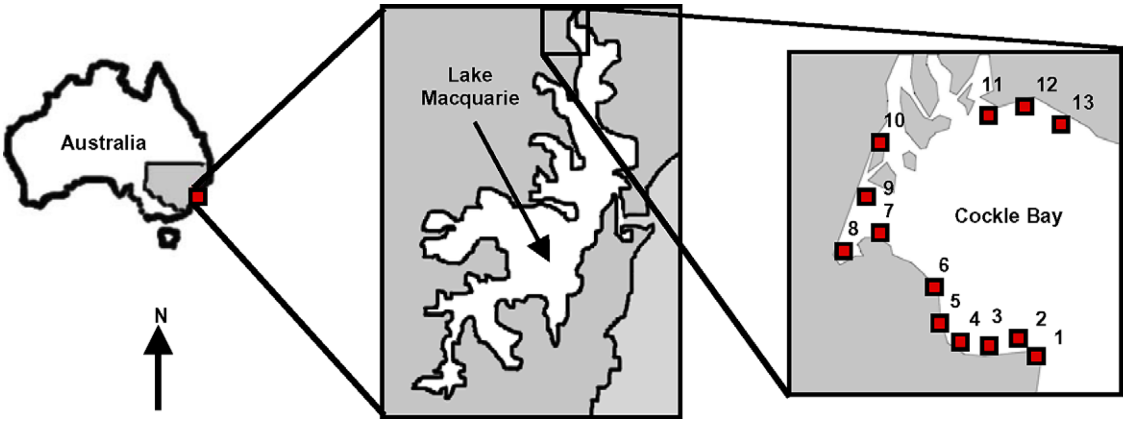

Fig. 1. The sediment collection sites in Lake Macquarie, New South Wales, Australia. The bulk sediments for metal release experiments were collected from Site 6 (GPS co-ordinates 0370303, 6351070 WGS84).