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## 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 3000mgkg<sup>-1</sup> (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 (5.58.0) and sediment disturbance (by physical mixing) than by changes in dissolved oxygen concentration (38mg/l) or salinity (1545 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

Effect, overlying, water, dissolved, oxygen, salinity, sediment, disturbances, metal, release, sequestration, from, metal, contaminated, marine, sediments, CMMB

## Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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**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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## 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<sup>-1</sup> (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 to 8.0) and sediment disturbance (by physical mixing) than by changes in dissolved oxygen concentration (3 to 8 mg/L) or salinity (15 to 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-d 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.

**Key Words** – Metal release and sequestration, contaminated sediments, bioturbation and physical disturbance, sediment-metal bioavailability , physico-chemical parameters.

## 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 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; Simpson *et al.* 2002; Kristensen 2000). 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 (Simpson *et al.* 2004; Eggleton and Thomas 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-d period. These experiments were performed on bioturbated and non-bioturbated sediments, using the sediment ingesting bivalve *Tellina deltoidalis*. After 21 d 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 d were physically mixed and metal release to and sequestration from the overlying water were investigated for up to 9 d.

## **Materials and methods**

### *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 (Figure 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 (Figure 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 5 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, *Tellina 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 ( $16 \pm 1$  mm shell length) for metal bioavailability experiments.

#### *Analytical methods*

All chemicals were analytical reagent grade or equivalent analytical purity. High-purity Milli-Q deionised water ( $18 \text{ M}\Omega \text{ cm}^{-1}$ , Millipore) was used for all solutions. All glass and plastic-ware was cleaned by soaking in 10 % (v/v)  $\text{HNO}_3$  for >24 h followed by rinsing with Milli-Q water.

Dissolved oxygen (DO) and temperature measurements were made using a YSI 95 meter (Model 95/25 Ft) and salinity measurements using a WTW meter (LF 320) with a TetraCon 325 probe (both meters were calibrated following manufacturer instructions). Salinity measurements have been reported according to the Practical Salinity Scale of 1978 (PSS 78) as dimensionless values. A Sensorex Combination pH electrode (450C) with a Rex pH meter (Model pH $\beta$ -4) was used for all pH measurements (in the field and in the lab) and was calibrated against standardised pH 4 and 7 NIST buffers before use. Sediment oxidation-reduction potential (ORP or redox) was measured using a Metrohm AG 9109 Herisau Combined Pt-wire electrode with Ag/AgCl reference electrode and Rex pH meter (Model pH $\beta$ -4). The instrument was calibrated using Orion Application Solution ORP Standard 967961 and all redox readings corrected for  $E_{\text{H}}^{\text{Ref}} = -210 \pm 3 \text{ mV}$ , i.e. reported redox potentials are versus the hydrogen electrode,  $E_{\text{H}}^0 = 0 \text{ mV}$ . Redox measurements were made when stable potentials were achieved, 1-2 min after insertion of the probe into the top 5 mm of the test sediment.

All samples were filtered using acid-washed (2%  $\text{HNO}_3$ ) and rinsed (Milli-Q water)  $0.45 \mu\text{m}$  cellulose nitrate membrane syringe filters (25 mm, Minisart, Sartorius). In all experiments, the dissolved metals fraction was defined as the metals passing through a  $0.45 \mu\text{m}$  filter, however, a portion of the metals measured in the overlying water may have been colloids. Dissolved metal concentrations were determined by inductively coupled argon plasma-atomic emission

spectrometry (ICP-AES) (Spectroflame EOP, Spectro Analytical Instruments) according to Simpson *et al.* (2002). Detection limits for reporting ICP-AES analyses of metals in seawater (acidified 0.2 % (v/v) HNO<sub>3</sub>) were 3-10 µg/L for Cd, Cu, Fe, Mn, Pb and Zn.

Total organic carbon (TOC) analyses in sediments were made using a high temperature TOC analyser (Dohrmann DC-190) following the removal of inorganic carbon (carbonates and bicarbonates) by acidification with 1 M HCl until effervescence was completed.

Sediment particle size fractionation was made by wet sieving the sediments through 1000, 250, and 63 µm mesh. Acid-volatile sulfide (AVS) in sediments was determined in bulk sediments from sediment cores using the methylene blue based rapid screening method developed by Simpson (2001). Total particulate metals (TPM, *aqua regia* digestion) and simultaneously-extracted metals (SEM, 1 M HCl) were determined as described in Simpson *et al.* (2002). Triplicate analyses of AVS and duplicate analyses of SEM and TPM were performed on sediments.

#### *Experimental set up for metal release assay*

Eight purpose-built chambers were constructed for the metal release experiments (Figure 2). Each main chamber was 30 cm × 30 cm × 8 cm deep (surface area = 0.090 m<sup>2</sup>). A 100 mL plastic container containing an aerator and magnetic stirring bar was positioned in the corner of each chamber, with its upper rim mid-way between the sediment and water surfaces. The overlying water was stirred and aerated for 0 - 15 min per hour, depending on the DO concentration required. Homogenised test sediment (4.00 ± 0.05 kg) was placed into the chamber and 1.5 L clean seawater was added (~1.7 cm water depth).

The temperature, pH, salinity and DO of the overlying waters were monitored daily. Over the 21-day test period, 20 mL samples of overlying waters were taken at the start of the test and then every second day. Overlying water samples were taken randomly from different sections of the experimental chamber, immediately filtered (0.45 µm), acidified to 0.2 % (v/v) HNO<sub>3</sub> and analysed for metals by ICP-AES. Overlying waters in all treatments were replenished with Milli-Q water following sampling to maintain constant water volume and required treatment salinity.

*Effect of pH, dissolved oxygen, salinity and bioturbation on metal release*

The effect of overlying water pH on metal release from sediments was investigated at high (pH  $8.1 \pm 0.2$ ), mid (pH  $7.2 \pm 0.2$ ) and low (pH  $6 \pm 1$ ) pH values (mean  $\pm$  standard deviation (SD)). Adjustments to pH were made by drop-wise addition of 1 M HCl to the water into the aeration chamber to allow rapid mixing and dispersion (15 min stirring by aeration after acid addition). For the low-pH experiments, continuous pH adjustment and stirring were necessary to overcome the strong pH-buffering capacity of the sediments. During the pH experiments the waters were  $19 \pm 1$  °C, salinity  $38 \pm 4$  PSU and  $8 \pm 1$  mg DO L<sup>-1</sup>. The low-pH experiment was duplicated.

The effect of overlying water DO on metal release from sediment was investigated at high ( $8 \pm 1$  mg DO L<sup>-1</sup>), mid ( $6 \pm 1$  mg DO L<sup>-1</sup>) and low ( $2.9 \pm 0.9$  mg DO L<sup>-1</sup>) concentrations. Variations in DO were obtained by altering the stirring and aeration rate: stirred continuously and aerated 15 min h<sup>-1</sup> to maintain high-DO, intermittently stirred and aerated (15 min h<sup>-1</sup>) to maintain mid-DO, and not stirred or aerated but covered with a black plastic lid (limiting light exposure and photosynthesis) to maintain low-DO conditions, respectively. During the DO experiments the waters were  $19 \pm 1$  °C, salinity  $35 \pm 3$  PSU and pH  $7.8 \pm 0.2$ . The low-DO experiment was duplicated.

The effect of salinity on metal release from sediments was investigated at high (35 PSU), mid (25 PSU) and low (15 PSU) salinity. Waters of varying salinity were maintained by addition of Milli-Q water to the seawater. During one of the first experiments unexpectedly rapid evaporation produced a very high (45 PSU) super-saline salinity treatment. During the salinity experiments the waters were  $19 \pm 1$  °C, pH  $8.1 \pm 0.2$  and  $8 \pm 1$  mg DO L<sup>-1</sup>.

To investigate the effect of bioturbation on metal release from sediments, 160 benthic bivalves, *T. deltoidalis*, were added to the sediment chambers. During the bioturbation experiments the waters were  $19 \pm 2$  °C, pH  $7.7 \pm 0.2$ , salinity  $35 \pm 3$  PSU and  $8 \pm 1$  mg L<sup>-1</sup> DO. After 21 days, all bivalves were removed from sediment by hand. The bioturbation experiment was duplicated.

*Effect of physical disturbance on metal release*

After the initial 21-day release period, sediments and overlying waters for all chambers were hand mixed for 10 minutes until an homogeneous black slurry was obtained. Water samples were taken and analysed for dissolved metals every few hours for 48 h, then every second day for six days. Water samples collected during the first 4 h after mixing were centrifuged (10 min, 2400 rpm) to remove the large quantity of suspended particles and the supernatant was filtered (0.45 µm) before metals analysis.

#### *Biological availability of the sediment bound metals*

In addition to analysis of total particulate and simultaneously-extractable metals, the biological availability of the sediment bound metals was also investigated. Twenty-five sediment ingesting *T. deltoidalis* were exposed to metal contaminated sediments, and a further 25 were exposed to control sediments, for 21 days according to the metal release assay set up described above, to assess the biological availability of sediment metals by comparative bioaccumulation. During these experiments the overlying waters were maintained at 18.5±0.5 °C, pH 8.0±0.5, salinity 35±3 and 8.0±0.5 mg DO L<sup>-1</sup>.

Metal concentrations in soft tissues were determined as described in King *et al.* (2004). In brief, animals were depurated, tissues dried, digested in nitric acid then hydrogen peroxide, diluted with Milli-Q water and metal concentrations were measured by ICP-AES. For quality control purposes, each batch of samples analysed included one blank (Milli-Q water) and two samples of an oyster tissue standard reference material (SRM 1566b, National Institute of Standards & Technology).

Metal bioavailability data was log<sub>10</sub>-transformed and Analysis of Variance (ANOVA) was used to test for differences in the concentration of cadmium, copper, lead and zinc within the whole soft tissue masses between the control and metal-contaminated sediments. All data figures were prepared using Microsoft® Excel 2000.

## **Results**

### *Sediment characteristics*

During sediment collection the overlying waters had temperatures of 22-27°C, pH of 7.8 - 8.2, salinity of 32.2 - 37.2 PSU and DO concentrations of 6.0 - 8.7 mg L<sup>-1</sup>. Surface (0-5 cm)

and depth (10-15 cm) sediments had similar pH and redox properties, pH was 6.8-7.8 at the surface and 6.8-8.1 at depth, and redox potential was -60 to 130 mV at the surface and -60 to 108 mV at depth. TPM (*aqua regia*) and SEM (1 M HCl) concentrations of Cd, Cu, Pb and Zn in the sediments are shown in Figure 3, along with the Australian sediment quality guideline (SQG) values for these metals, 1.5, 65, 50, 200 mg kg<sup>-1</sup>, respectively (ANZECC/ARMCANZ 2000). The maximum measured metal concentrations were 86 mg kg<sup>-1</sup> Cd, 240 mg kg<sup>-1</sup> Cu, 700 mg kg<sup>-1</sup> Pb, and 3000 mg kg<sup>-1</sup> Zn. Sediment concentrations were fairly consistent around the study area, with the greatest variability found at sites 7-10, in the western corner of the bay, which receives direct water flow from the metal-contaminated creek (Cockle Creek).

Acid volatile sulfide (AVS) is considered to be a major metal-binding phase in anoxic sediments, and pore water metal concentrations are predicted to remain low when there is a molar excess of AVS over SEM (Di Toro *et al.* 1992; Simpson 1998). Although many of the sediments appeared to be sub-oxic, most of the sediments had a molar excess of AVS over SEM (Figure 4). In replicate sediment cores from a single site, greater variations in concentrations of AVS (factor of 1.5-7.2) were measured than the respective SEM (factor of 1.1-2.5). It was expected that the deeper sediments (10-15 cm depth) would be more anoxic and contain greater concentrations of AVS than the surface sediments (0-5 cm depth), but this was observed for only 50% of the sites (Figure 4). This may indicate that in the deeper sediments contained more pyritic sulfide phases that are not extracted by the AVS method (Simpson *et al.*, 1998). In addition, greater differences might have been observed if higher resolution depth profiles were undertaken for AVS analyses. In general, the sediments were quite heterogenous with respect to AVS, probably due to the burrowing activities of organisms that introduce oxygen at depth. Particulate iron concentrations (SEM-Fe) were typically 10-200 µmol g<sup>-1</sup> and AVS analyses indicated that 10-20% of that Fe was present as iron sulfide, with the remainder expected to be present in iron hydroxide and carbonate phases (Stumm and Morgan, 1996).

Sediments from Site 6 were used to investigate the effects of pH, salinity, DO and sediment disturbance on metal release rates. This sediment was silty (73% <63 µm, 18% 63-

250  $\mu\text{m}$ , 9% 250-1000  $\mu\text{m}$ ) with TOC concentrations of 24-44  $\text{mg kg}^{-1}$  (dry weight) and an excess of SEM over AVS of 1-7  $\mu\text{mol g}^{-1}$ . SEM concentrations in the bulk Site 6 sediment were 21  $\text{mg kg}^{-1}$  Cd, 35  $\text{mg kg}^{-1}$  Cu, 250  $\text{mg kg}^{-1}$  Pb, and 950  $\text{mg kg}^{-1}$  Zn. In the <63/63-250/250-1000  $\mu\text{m}$  particle size fractions the SEM concentrations (in  $\text{mg kg}^{-1}$ ) were 18/22/14 for Cd, 37/19/14 for Cu, 253/119/84 for Pb, and 905/819/587 for Zn. The finest sediment fraction had the highest metal concentrations of Cu, Pb and Zn and was expected to be the most easily resuspended by water currents or bioturbation and the most easily ingested by bivalves. Furthermore, while the highest Cd concentration was found in 63-250  $\mu\text{m}$  sediment, the greatest amount of Cd is present in the <63  $\mu\text{m}$  fraction as it comprises 73% of the total sediment volume, compared to 18% for the 63-250  $\mu\text{m}$  fraction.

#### *Effect of pH and physical disturbances on metal release from sediments*

Little or no release of Cd, Cu, Pb or Zn was observed for the high- and mid-pH experiments, but for low-pH experiments Pb and Zn concentrations in the overlying waters were high (Figure 5). Dissolved copper was <3  $\mu\text{g L}^{-1}$  throughout all experiments. Dissolved cadmium was <3  $\mu\text{g L}^{-1}$  during the high- and mid-pH experiments, but in the low-pH experiments was 4-13  $\mu\text{g L}^{-1}$  over the 6-18 day period and 40-50  $\mu\text{g L}^{-1}$  for days 19 and 21. The release of lead was only significant in the low-pH experiments with lead concentrations of 100-370  $\mu\text{g L}^{-1}$  measured on days 19 and 20 (Figure 5). Zinc releases were observed in the mid-pH and low-pH experiments, with average zinc concentrations of 65  $\mu\text{g L}^{-1}$  during the low-pH experiment and maximum zinc concentrations of 1600  $\mu\text{g L}^{-1}$  in the low-pH experiments (Figure 5). During the first 21 days of the experiments, release of Mn was observed only in the low-pH experiments and release of Fe was observed in the low-pH and mid-pH experiments (Figure 5). The increase in dissolved metal concentrations with time reflects a steady release rate as the metals in the sediment-water system equilibrated with the new overlying water condition.

At day 21, the sediments were disturbed by physical mixing and then left undisturbed for a further nine days (Figure 5). Upon sediment disturbance, dissolved iron concentrations increased in the high-pH experiments and decreased in the mid-pH and low-pH experiments,

while dissolved manganese concentrations increased in the mid- and high-pH experiments and decreased in the low-pH experiments. Following the sediment disturbance the dissolved Pb and Zn concentrations remained low in the high-pH experiments, but increased in the mid-pH experiments. For the low-pH experiments, dissolved Pb and Zn concentrations decreased immediately following sediment disturbance, before increasing again after 24 h, once the majority of the suspended particles from the sediment disturbance had settled.

During the eight days following the sediment disturbance, the metal concentrations in the overlying waters generally returned to concentrations measured before the disturbance period, indicating that the release of metals to the overlying waters was only temporary. In the low-pH experiments, the dissolved concentrations of Fe, Pb and Zn were similar to those measured before the disturbance period within 72 h. In the mid-pH experiments, dissolved Mn and Pb concentrations remained elevated compared to concentrations in the overlying waters before disturbance.

#### *Effect of dissolved oxygen and physical disturbances on metal release from sediments*

In all DO experiments the overlying water was pH 8, salinity  $35 \pm 3$  PSU and dissolved Cd, Cu, Pb and Zn were below detection limits until the sediments were disturbed. These results were consistent with the high pH experiments discussed above. Sediment disturbance resulted in the release of lead to the overlying water in the low- and mid-DO experiments, and was greater in low-DO experiments (Figure 6). Following the initial release of lead, immediately after sediment disturbance the dissolved lead concentrations decreased but remained greater than pre-disturbance concentrations (below detection). Following sediment disturbance, dissolved zinc concentrations generally remained  $< 5 \mu\text{g L}^{-1}$  in the high- and mid-DO experiments, but were  $50 \pm 40 \mu\text{g L}^{-1}$  ( $150 \mu\text{g L}^{-1}$  maximum) in the low-DO experiments. Dissolved copper concentrations remained  $< 3 \mu\text{g L}^{-1}$  in the high-DO experiments, but were  $5\text{--}20 \mu\text{g L}^{-1}$  for the 24-h period following sediment disturbance in the mid- and low-DO experiments. Dissolved cadmium remained  $< 3 \mu\text{g L}^{-1}$  in all DO experiments.

#### *Effect of salinity on metal release from sediments*

Changes in overlying water salinity are most likely to occur due to short-term freshwater input following rain. In the experiments that started with a salinity of 15 or 25PSU, the overlying water salinity returned to  $35\pm3$  within 30 h of the experiments commencing. The strong salinity-buffering capacity of the sediments and the rapid rate at which overlying waters returned to the normal water salinity indicated that any overlying water salinity changes would be only temporary for these sediments. In the natural setting, mixing with surrounding waters would further increase the dilution rate of freshwater inputs. There was no significant difference between the rates of metal release in these experiments. In the evaporated waters experiment with salinity of 45 PSU (maintained throughout the 29-day experiments), there was no difference in metal release rates compared to experiments where the salinity was maintained at 35 (both of these experiments also contained bivalves).

#### *Effect of bioturbation on metal release from sediments*

There was little change between the release of Pb and Zn from the sediments with or without the bioturbating bivalve *T. deltoidalis*, however, differences were observed in the release of Fe and Mn. During the 21-d metal release period, dissolved metal concentrations in the overlying waters were (mean $\pm$ SD,  $\mu\text{g L}^{-1}$ )  $245\pm270$  (Fe),  $6\pm4$  (Mn),  $25\pm8$  (Pb), and  $33\pm21$  (Zn) in the original sediments, and  $800\pm620$  (Fe),  $96\pm91$  (Mn),  $32\pm28$  (Pb), and  $55\pm42$  (Zn) in the sediments where *T. deltoidalis* was added. Cadmium and copper concentrations under these natural environmental conditions (pH 8.0, salinity of 35 PSU,  $8.0\text{ mg DO L}^{-1}$ ) were below detection.

Furthermore, the physical disturbance of the sediment that occurred when the bivalves were removed from the bioturbation treatments on day 21 was very similar to the disturbance by hand mixing of the original pH, DO and salinity metal release tests. This allowed a direct comparison between the effect of physical disturbance on the original and the bivalve-bioturbated sediments (now both in the absence of bivalves). The dissolved metal concentrations ( $\mu\text{g L}^{-1}$ ) in the overlying waters during the next 48 h were (mean $\pm$ SD)  $840\pm690$  (Fe) and  $300\pm300$  (Mn) in the original sediment, and  $640\pm325$  (Fe) and  $140\pm110$

(Mn) in the bivalve-bioturbated sediment. Concentrations of Pb and Zn did not change significantly, and Cu and Cd concentrations were below detection.

#### *Metal bioavailability in contaminated sediments*

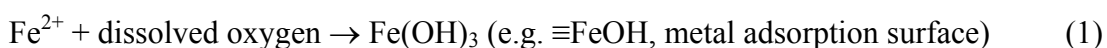
No mortality (100% survival) of *T. deltoidalis* occurred over the 21-day exposure to the contaminated sediments. This was consistent with previous studies that determined lowest observable effect concentrations (LOEC's) of  $>100 \text{ mg kg}^{-1}$  for Cd, Ni and  $>1000 \text{ mg kg}^{-1}$  for Cu, Pb, Zn, for *T. deltoidalis* in 10-d whole-sediment exposures (King *et al.*, unpublished results).

Following 21-day sediment exposures, *T. deltoidalis* accumulated significantly higher ( $P < 0.001$ ,  $n=20$ ) concentrations of cadmium, lead and zinc in their tissues from metal contaminated sediments, in comparison to the control sediments (Table 1, Figure 7). No significant differences were observed for copper bioaccumulation. Measured metal concentrations in the oyster tissue SRM were in reasonable agreement with certified values ( $n=10$ ). Measured (certified) concentrations (mean $\pm$ SD,  $\mu\text{g g}^{-1}$  dry weight) of cadmium  $2.60\pm0.01$  ( $2.48\pm0.08$ ), copper  $71.6\pm1.6$  ( $78.5\pm0.8$ ), and zinc  $1420\pm46$  ( $1540\pm8$ ). Lead recoveries were significantly above the certified values  $0.49\pm0.08$  ( $0.308\pm0.009$ )  $\mu\text{g g}^{-1}$  dry weight and thus the lead concentrations presented here can only be considered for relative differences between the treatment and control.

## **Discussion**

#### *Effect of pH and physical disturbances on metal release*

The metals released from the sediments appeared to be scavenged from the overlying water by adsorbing to resuspended particles and iron and manganese (hydr)oxide solid phases (e.g.  $\text{Fe}(\text{OH})_3$ ,  $\text{FeOOH}$ ,  $\text{MnO}_2$ ), which were formed through the oxidative precipitation of dissolved Fe(II) and Mn(II) cations that were simultaneously released from the pore waters (equations 1 and 2).



355

356 The influence of pH on these reactions is two-fold: pH influences (i) the rate of oxidation  
357 of Fe(II), and (ii) the binding of metals to organic-, iron- and manganese-based metal-binding  
358 phases. Both of these processes result in faster rates of metal scavenging in waters with high  
359 pH and they concur with the observed results (Figure 5). Santana-Casiano *et al.* (2004) found  
360 that the half life of  $1000 \mu\text{g L}^{-1}$  Fe(II) in seawater (36.7 salinity, 25 °C, air saturated) was ~0.8  
361 min at pH 8, ~20 min at pH 7 and >300 min at pH 6. The rate of oxidation of Mn(II) and  
362 precipitation as  $\text{MnO}_2$  is very slow in the pH range 5-9 (Stumm and Morgan 1996).

363 In the absence of sediment disturbance, the reactions depicted in equations 1 and 2 will be  
364 fastest at the sediment-water interface, where oxygen penetration is greatest and the oxidative  
365 precipitation of iron oxyhydroxide phases occurs most rapidly. Following sediment  
366 disturbance, resuspended particulates that contain metal-binding sites in the form of organic-  
367 carbon and iron were expected to be more important for scavenging released metals from the  
368 overlying water. A return to pre-disturbance metal concentrations occurred as the sediment  
369 particulates re-settled, and the sediment redox conditions and sediment-water equilibrium was  
370 re-established.

371 The pH experiments indicate that under high- and mid-pH conditions minimal metal  
372 release from sediments is observed even with considerable physical disturbance. At low pH  
373 (5.5-6) metal release is observable, however, instances of low pH are rare, and natural  
374 dilution and pH buffering would minimise effects to benthic biological organisms.

#### 375 *Effect of dissolved oxygen and physical disturbances on metal release*

376 The results indicated that when DO concentrations were lower, the rate of release of Fe(II)  
377 and Mn(II) from the pore waters was faster and steady-state concentrations in the overlying  
378 waters were higher (Figure 6). This observation is related to the slower rate of oxidative-  
379 precipitation and scavenging of these ions as they diffuse through the sediment-water  
380 interface. Immediately following sediment disturbance, the release of dissolved iron and  
381 manganese was greatest in the high-DO experiments. This was consistent with the sediments  
382 of the high-DO experiments having high concentrations of Fe(II) and Mn(II) in the

porewaters (Figure 6), but sediment disturbance (rather than diffusion) was required for its release to overlying waters. The effect of DO on metals in the overlying water appeared clearer for Mn than Fe, because of the slower oxidative precipitation of Mn(II) than Fe(II).

#### *Effect of bioturbation metal release*

The effect of bioturbating organisms on metal release from sediment was investigated by the addition of the benthic bivalve *T. deltoidalis* to sediments. The bivalve *T. deltoidalis* typically resides in the top 3-15 cm of sediments and feeds by sucking up sediment from the surface with one siphon, and discharging indigestible particles and faeces via the exhalant siphon to the sediment surface (Beesley *et al.* 1998).

While the sediment disturbance caused by bivalve bioturbation was small and continuous compared to the short but drastic physical disturbances of non-bioturbated sediments, the pattern of metal release, if not release concentrations, was consistent, with significant Fe and Mn, and minimal Pb and Zn release observable for both types of tests.

Furthermore, bioturbation results have similarities to the DO experiment results. Bioturbation, like low DO, increased the release of Fe and Mn from the sediment pore waters, and consequently porewater Fe and Mn concentrations in bioturbated sediments were lower than those in sediments without bioturbation. When physical disturbance occurred, a greater release of Fe and Mn occurred from the sediments without bioturbation due to the higher (trapped) porewater Fe and Mn concentrations.

#### *The bioavailability of the sediment-bound-metals*

The metal concentrations in bivalves exposed to contaminated sediments varied considerably, but were of similar magnitude to those typically observed for bioaccumulation studies (Table 1). Biokinetic studies using Cd and Cu radioisotopes have shown that *T. deltoidalis* would require >40 days exposure to reach steady-state body concentrations of these metals in sediments (King *et al.* 2005). It is possible that a longer exposure period would result in a greater metal bioaccumulation in bivalve tissues, and also produce less variable metal concentrations.

The accumulation of cadmium, lead and zinc in the benthic bivalve, *T. deltoidalis*, demonstrates the bioavailability of the metals in the contaminated sediments used in these tests. The molar excess of SEM over AVS, and the continued cycling of the metals between the pore waters and the surface sediments due to the bioturbation process are likely to be a key process maintaining the bioavailability of the metals in the sediments. The feeding of *T. deltoidalis* on the oxidised surface sediments is likely to be the major route of metal accumulation.

## Conclusions and summary

The release of metals from sediments (and pore waters) occurred during sediment disturbance, with significant releases during severe mixing and less significant releases from biological mixing. This study demonstrated that metal release from metal-contaminated sediments was influenced by iron and manganese redox chemistry. Larger releases into overlying waters occurred at lower pH (5.5) and DO (3 mg/L) as the sediment bound iron and manganese were reduced, with pH effecting release rates up to 10 fold greater than those for DO. Upon mixing the released and resuspended metals became oxidised, sequestered to particulate phases in the water column, and precipitated with the oxidised iron and manganese. At higher pH and DO (pH 8.0 and DO 8.0 mg L<sup>-1</sup>) there were faster oxidation rates of Fe and Mn (and hence faster rates of metal precipitation), which generated lower dissolved metal concentrations in the overlying water. Hence in natural environments, the pH and dissolved oxygen of the overlying water will govern the rate at which released metals will be scavenged from the water column and returned to the sediment. During this study, for mid to high pH and DO conditions, the overlying water metal concentrations generally returned to pre-disturbance conditions within eight days, the metal release was only temporary. The accumulation of metals in the *T. deltoidalis* demonstrates the bioavailability of the metals in contaminated sediments, where the bioavailability is likely to be a result of the molar excess of SEM over AVS, and the continued cycling of the metals between the pore waters and the surface sediments due to the bioturbation process.

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443

444 **References**

- 445 ANZECC/ARMCANZ (2000). Sediment quality guidelines. Australia and New Zealand  
 446 Environment and Conservation Council & Agriculture and Resource Management  
 447 Council of Australia and New Zealand.
- 448 Beesley, P., Ross, G. L., and Wells, A. J. B. (1998). Mollusca: The Southern Synthesis. Fauna  
 449 of Australia. Vol 5 Part A. (CSIRO Publishing: Melbourne).
- 450 Burdige, D. J. (1993). The biochemistry of manganese and iron reduction in marine  
 451 sediments. *Earth Sci Rev* **35**, 249-284.
- 452 Calmano, W., Hong, J., and Förstner, U. (1993) Binding and mobilisation of heavy metals in  
 453 contaminated sediments affected by pH and redox potential. *Water SciTechnol* **28**, 223-  
 454 235.
- 455 Chapman, P. M., Wang, F. Y., Janssen, C., Persoone, G., and Allen, H. E. (1998).  
 456 Ecotoxicology of metals in aquatic sediments: binding and release, bioavailability, risk  
 457 assessment, and remediation. *Can J Fish Aquat Sci* **55**, 2221-2243.
- 458 Ciutat, A., and Boudou, A. (2003). Bioturbation effects on cadmium and zinc transfers from a  
 459 contaminated sediment and on metal bioavailability to benthic bivalves. *Environ Tox*  
 460 *Chem* **22**, 1574-1581.
- 461 Di Toro, D. M., Mahony, J. D., Hansen, D. J., Scott, K. J., Carlson, A. R., and Ankley, G. T.  
 462 (1992). Acid volatile sulfide predicts the acute toxicity of cadmium and nickel in  
 463 sediments. *Environ Sci Technol* **26**, 96-101.
- 464 Eggleton, J., and Thomas, K. V. (2004). A review of factors affecting the release and  
 465 bioavailability of contaminants during sediment disturbance events. *Environ International*  
 466 **30**, 973-980.
- 467 King, C. K., Dowse, M. C., Simpson, S. L., and Jolley, D. F. (2004). An assessment of five  
 468 Australian polychaetes and bivalves for use in whole-sediment toxicity tests: toxicity and  
 469 accumulation of copper and zinc from water and sediment. *Arch Environ Con Tox* **47**,  
 470 314-323.
- 471 King, C. K., Simpson, S. L., Smith, S. V., Stauber, J. L., and Batley, G. E. (2005). Short term  
 472 accumulation of Cd and Cu from water, sediment and algae by the amphipod *Melita*  
 473 *plumulosa* and the bivalve *Tellina deltoidalis*. *Mar Ecol-Prog Ser* **287**, 177-188.
- 474 Kristensen, E. (2000). Organic matter diagenesis at the oxic/anoxic interface in coastal marine  
 475 sediments, with emphasis on the role of burrowing animals. *Hydrobiologia* **426**, 1-24.
- 476 Riedel, G. F., Sanders, J. G., and Osman, R. W. (1997). Biogeochemical control on the flux of  
 477 trace elements from estuarine sediments: Water column oxygen concentrations and  
 478 benthic infauna. *Estuar Coast Shelf S* **44**, 23-38.
- 479 Santana-Casiano, J. M., González-Dávila, M., and Millero, F. J. (2004). The oxidation of  
 480 Fe(II) in NaCl-HCO<sub>3</sub> and seawater solutions in the presence of phthalate and salicylate  
 481 ions: a kinetic model. *Mar Chem* **85**, 27-40.
- 482 Simpson, S. L. (2001). A rapid screening method for acid-volatile sulfide in sediments.  
 483 *Environ Tox Chem* **20**, 2657-2661.
- 484 Simpson, S. L. (2005). An exposure-effect model for calculating copper effects  
 485 concentrations in sediments with varying copper binding properties: a synthesis. *Environ*  
 486 *Sci Technol* **39**, 7089-7096.

487 Simpson, S. L., and Batley, G. E. (2003). Disturbances to metal partitioning during toxicity  
488 testing iron(II)-rich estuarine pore waters and whole sediments. *Environ Tox Chem* **22**,  
489 424-432

490 Simpson, S. L., Angel, B. M., and Jolley, D. F. (2004). Metal equilibration in laboratory-  
491 contaminated (spiked) sediments used for the development of whole-sediment toxicity  
492 tests. *Chemosphere* **54**, 597-609.

493 Simpson, S. L., Apte, S. C., and Batley, G. E. (1998). Effect of short-term resuspension  
494 events on trace metal speciation in polluted anoxic sediments. *Environ Sci Technol* **32**,  
495 620-625.

496 Simpson, S. L., Pryor, I. D., Mewburn, B. R., Batley, G. E., and Jolley, D. F. (2002).  
497 Considerations for capping metal-contaminated sediments in dynamic estuarine  
498 environments. *Environ Sci Technol* **36**, 3772-3778.

499 Stumm, W., and Sulzberger, B. (1992). The cycling of iron in natural environments:  
500 considerations based on laboratory studies of heterogeneous redox processes. *Geochim*  
501 *Cosmochim Ac* **56**, 3233-3257.

502 Stumm, W., and Morgan, J. J. (1996). 'Aquatic Chemistry. Chemical Equilibria and Rates in  
503 Natural Waters.' 3rd Edn. John Wiley: New York.

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List of Figure and Table captions.

Figure 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 coordinates 0370303, 6351070 WGS84).

Figure 2. Schematic representation of metal release experimental setup. Each container was  $30 \times 30 \times 8$  cm, contained 4 kg of sediment and 1.5 L overlying water.

Figure 3. TPM ( $\bigcirc\bullet$ ) and SEM ( $\blacktriangle\triangle$ ) concentrations for 0-5 cm surface ( $\bigcirc\triangle$ ) and 10-15 cm depth ( $\blacktriangle\bullet$ ) sediments from contaminated sediments at Cockle Bay. The dashed line represents the Australian sediment quality guideline value (ISQG-low value, ANZECC/ARMCANZ, 2000). The standard error (bars shown) between replicate analyses was generally 10-30%.

Figure 4. Concentrations of AVS ( $\square\triangle$ ) and the molar AVS-SEM difference ( $\blacksquare\blacktriangle$ ) in the 0-5 cm surface ( $\triangle\blacktriangle$ ) and 10-15 cm depth ( $\square\blacksquare$ ) sediments from contaminated sediments at Cockle Bay. Replicates shown at sites 4, 5, 6, 7 and 13. The standard error between duplicate analyses was generally 10-30%.

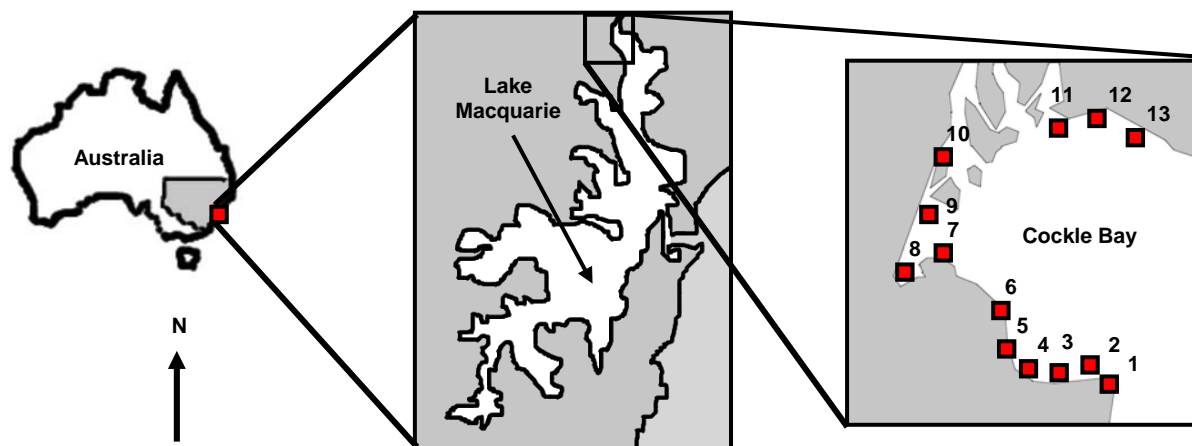
Figure 5. Concentrations of dissolved Fe, Mn, Pb, and Zn in the overlying waters over the 29-d metal-release experiments at low-pH ( $6\pm1$ ) ( $\bigcirc$ ), mid-pH ( $7.2\pm0.2$ ) ( $\blacksquare$ ) and high-pH ( $8.1\pm0.2$ ) ( $\triangle$ ). Error bars represent standard errors for duplicate experiments. On day 21 the sediment was disturbed. Data below the detection limit, represented by the dashed line, are not shown.

Figure 6. Concentration of dissolved Fe, Mn, and Pb in the overlying waters (pH 8) over the 29-d metal-release experiments at low-DO ( $3 \text{ mg L}^{-1}$ ) ( $\bigcirc$ ), mid-DO ( $6 \text{ mg L}^{-1}$ ) ( $\blacksquare$ ) and high-DO ( $8 \text{ mg L}^{-1}$ ) ( $\triangle$ ) concentrations. Error bars represent standard errors for duplicate experiments. On day 21 the sediment was disturbed. Data below the detection limit, represented by the dashed line, are not shown.

Figure 7. Concentration of cadmium (mg/kg, dry mass) in the soft tissue mass of *Tellina deltoidalis* following 21-day exposure to control (■) and contaminated (△) bulk sediments. Overlying waters were maintained at  $18.5 \pm 0.5^{\circ}\text{C}$ , pH  $8.0 \pm 0.5$ , salinity  $35 \pm 3\text{‰}$  and  $8.0 \pm 0.5 \text{ mg DO L}^{-1}$ .

Table 1. Metal concentrations in test sediments and *T. deltoidalis* following 21-day exposure. Control and contaminated sediments, mean  $\pm$  std error ( $\text{mg kg}^{-1}$ , dry mass).

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Figure 1.

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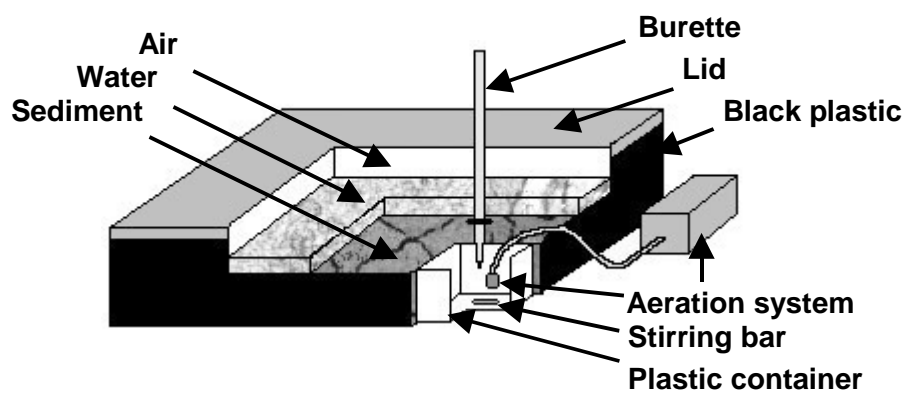
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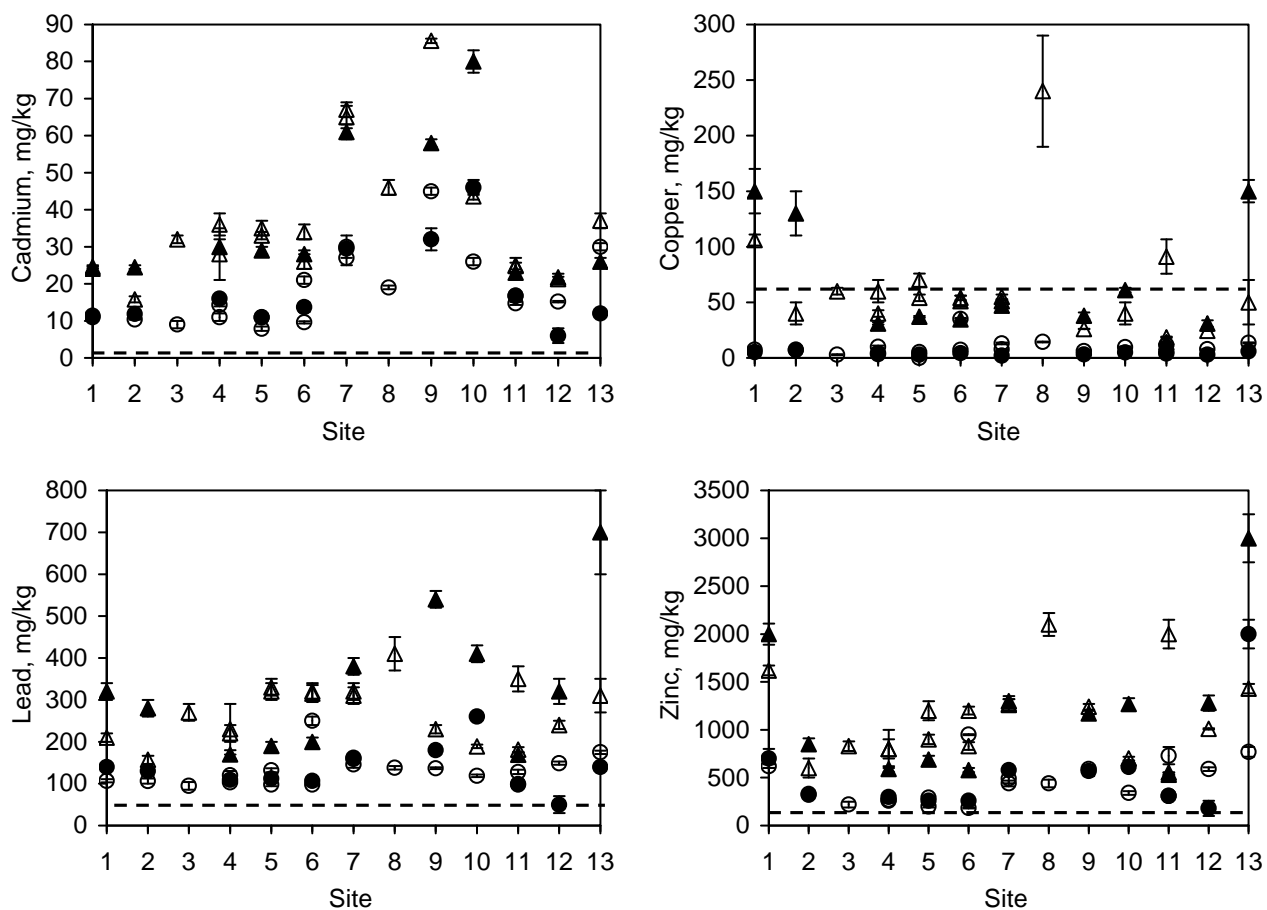
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Figure 2.

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**Figure 3.**

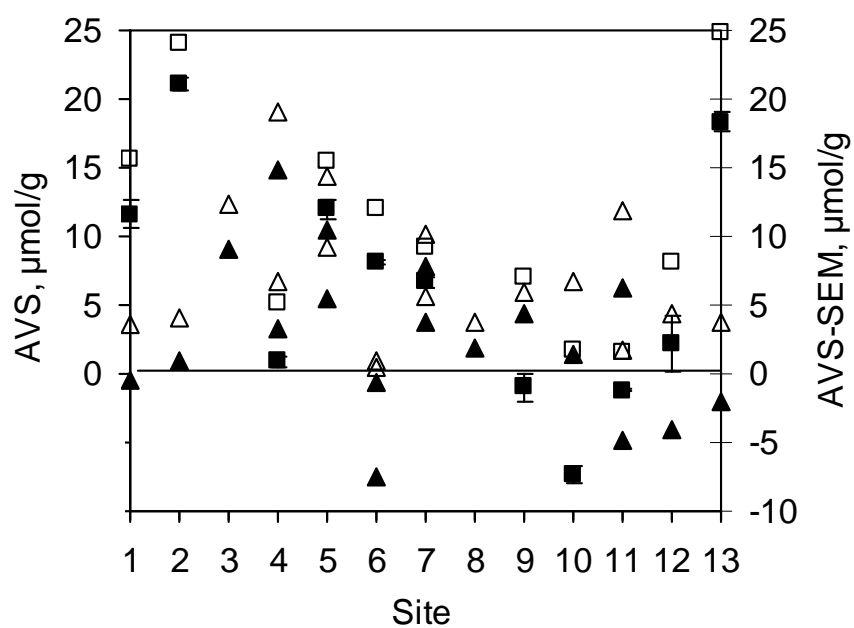


Figure 4.

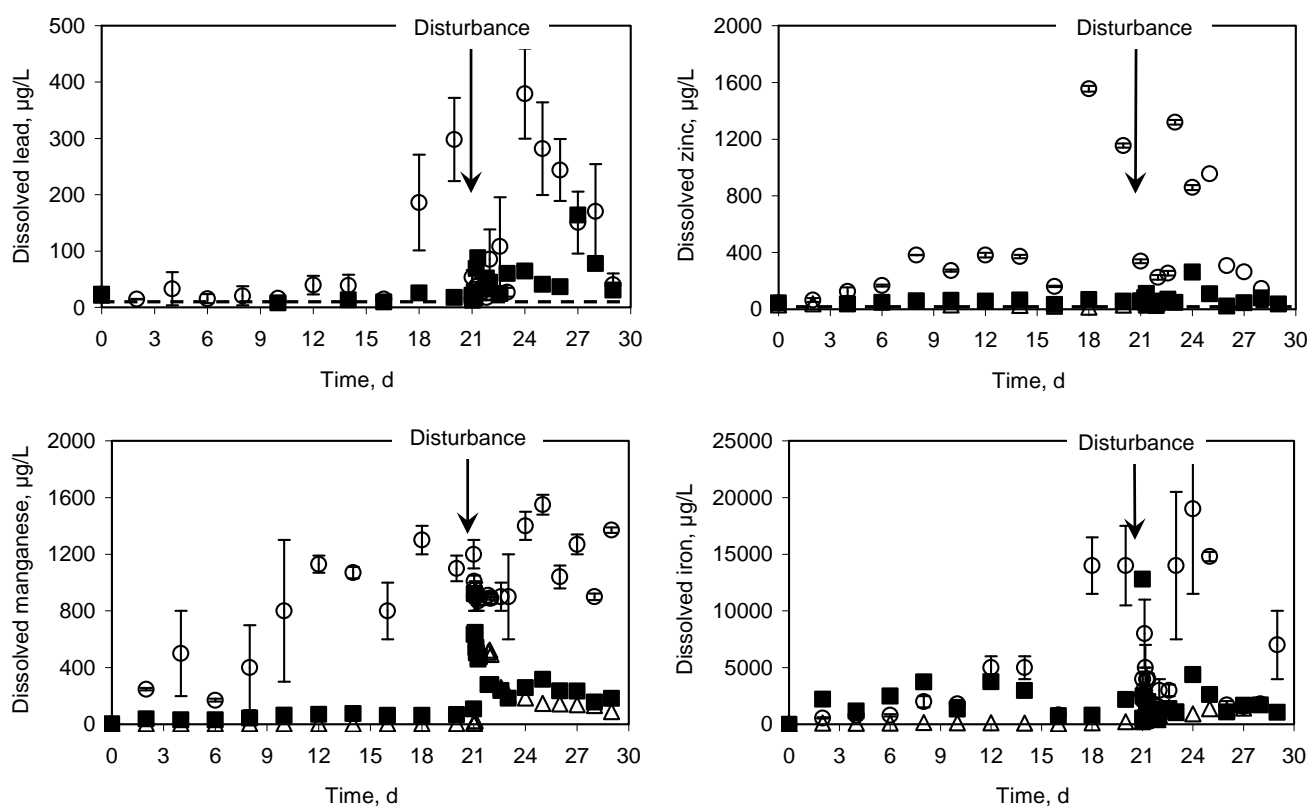
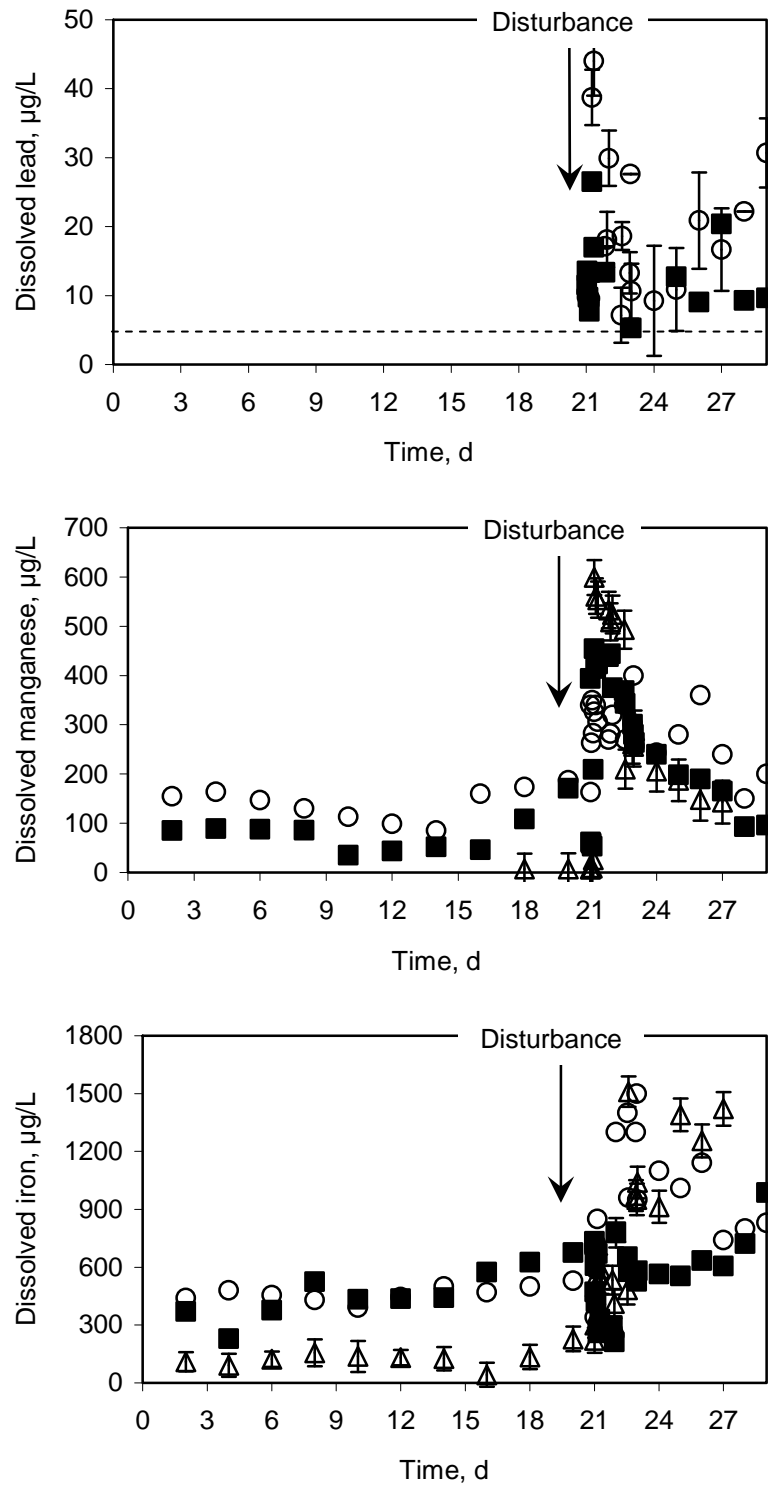
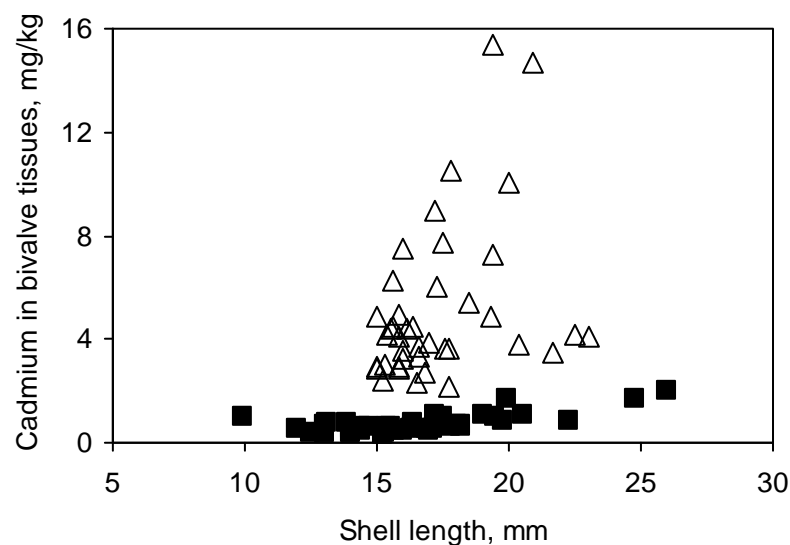


Figure 5.



**Figure 6.**



**Figure 7.**

**Table 1.**

Metal	Total metals in sediment		Bivalve tissue concentrations		*Significance
	Boronia Park (n=5)	Cockle Bay (n=6)	Boronia Park (n=20)	Cockle Bay (n=20)	Differences in bivalve metals
Cadmium	0.6 ± 0.1	25.5 ± 0.5	0.73 ± 0.08	5.1 ± 0.7	P < 0.001
Copper	25 ± 10	51 ± 3	220 ± 30	290 ± 45	P = 0.161
Lead	35 ± 15	314 ± 4	26 ± 3	55 ± 8	P < 0.001
Zinc	90 ± 20	1200 ± 60	230 ± 20	370 ± 50	P < 0.001

\* Significant differences between log-transformed data from Boronia Park and Cockle Bay bivalve tissues.