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Abstract

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Keywords

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Considerations for Capping Metal-Contaminated Sediments in Dynamic Estuarine Environments

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The effects of tides, bioturbating organisms and periods of anoxia on metal fluxes from contaminated harbour sediments in a shallow tidal estuarine bay were studied, together with capping technology options for the containment of metal contaminants. Zinc fluxes from the sediments were high, ranging from 10 to 89 mg Zn /m^2/day. In the absence of capping, experiments in corer reactors showed that simulated tidal processes increased zinc fluxes 5-fold. Fluxes were also greater in the presence of sediment-dwelling organisms. If organisms were removed, and recolonising organisms later added, their bioturbation activities initially lowered zinc fluxes, but fluxes gradually reached steady state at the higher levels seen previously. Capping materials physically isolate contaminated sediments, provide a binding substrate for metals released from the sediment, and importantly create an anoxic environment below the cap, that stimulates the formation of insoluble metal sulfides. Clean sediment (5 mm) was the most effective capping material in reducing zinc fluxes. Zeolite/sand mixtures (10 mm) also greatly reduced these fluxes, but significant breakthrough of zinc occurred after two weeks. Sand (20 mm) was not effective. The presence of organisms disturbed capping materials and increased zinc fluxes. Installed capping materials should have depths of >30 cm to minimise organisms burrowing to contaminated sediments beneath.

Key Words— Sediments, metals, capping, barriers, fluxes.

Introduction

Harbours in most cities of the world have sediments that are contaminated with heavy metals and other contaminants as a legacy of historical industrial discharges and urban stormwater runoff. Only recently has attention been given to the impacts of contaminants in sediments on sensitive benthic organisms, with guidelines being proposed that are designed to protect these species (*1*). Where such guidelines are exceeded, environmental agencies are faced with the dilemma of determining how, if at all, to remediate the contamination.

Remediation options for metal contaminated sediments include:

(i) doing nothing, and allowing diffusive losses of contaminants to the overlying waters with erosion dispersing contaminants or natural sedimentation gradually capping them (the easiest and cheapest option),

(ii) modification of environmental conditions (e.g. pH neutralisation, bacterial remediation) to minimize metal release,

(iii) capping using clean sediment, sand or geotextile materials (e.g. zeolite), to physically isolate the sediments from the overlying waters, and

(iv) dredging and disposal of the contaminated sediments (at sea or in landfill) (*2-4*).

In advance of remediation considerations, some understanding is required of the factors affecting contaminant mobility and bioavailability in the sediments. Compared to sediments in freshwater environments, estuarine sediments are subjected to tidal cycles that cause fluctuations in overlying water depth, salinity, temperature and dissolved oxygen concentration. These changes effect the penetration of oxygen and the redox conditions within estuarine sediments, resulting in significant changes to metal speciation and to the flux of metals from sediments (*5-11*). Burrowing organisms, which bioturbate and bioirrigate the sediments, are also expected to influence metal speciation and fluxes, and their behaviour will, in turn, be effected by tides (*5, 8, 12-15*).

The dynamic equilibrium between oxidized and reduced forms of iron, manganese and sulfur will play a crucial role in controlling metal speciation and fluxes, particularly in estuarine environments (*5, 15, 16*). These elements often co-exist in apparently non-equilibrium conditions, where small disturbances to conditions in microenvironments in the sediments can cause rapid changes to metal oxidation states and partitioning (*16, 17*). Recent high-resolution studies of the sediment-water interface have indicated that the sharp concentration maximum for many trace metals occurring in the top 1.5-3 mm of the sediments may drive the metal fluxes to the overlying waters (*18*). Because this zone coincides with the depth at which iron and manganese (hydr)oxides are being reductively solubilised, trace metal concentrations at this depth are expected to be strongly affected by iron/manganese redox chemistry.

The dynamic nature of shallow estuarine environments may constrain remediation options. Natural recovery will depend on deposition and erosion rates, and the modification of environmental conditions is difficult due to the large scale of these open systems. Capping materials, used as barriers to prevent contaminant release, must maintain adsorptive properties over fluctuating temperatures, salinities and dissolved oxygen concentrations. Dredging and disposal of contaminated sediments is an expensive option. Furthermore, because of the importance of estuaries as highly productive ecosystems, it is necessary that changes to sediment structure due to remediation should not inhibit recolonization by sediment-dwelling plants and organisms.

This study uses corer-reactors (*19*) to examine the effects of tides, bioturbating organisms and periods of anoxia on metal fluxes from estuarine sediments in Five Dock Bay, a severely metal-contaminated site in Sydney Harbour, Australia. Having characterized the dynamics of metal mobilization, the effectiveness of capping technology options for the

containment of metal contaminated sediments in this environment was investigated using the same reactor systems.

Materials and Methods

General methods and reagents. All glass and plasticware was cleaned by soaking in 10% (v/v) HNO_3 (Trace Pur, Merck, Darmstadt, Germany) for >24 h followed by three rinses with deionised water (Milli-Q). All laboratory-ware used for dissolved metals sampling and analysis was cleaned in a Class-100 laminar flow cabinet (metal-free HWS, Clyde-Apac). High-purity (18 MΩ·cm) Milli-Q deionised water (Millipore, Australia) was used to prepare all solutions. All chemicals were AR grade or equivalent analytical purity. Clean seawater was collected from Cronulla, NSW, Australia.

Measurements of pH were calibrated against standard NBS buffers and redox potential versus the standard hydrogen electrode. Salinity, temperature and dissolved oxygen measurements were made in accordance with the instrument manufacturer's instructions. Procedures for sediment organic carbon and size fractionation determinations have been described previously (*20*). Total suspended solids were analyzed according to standard methods (*21*). Acid-volatile sulfide (AVS) was determined according to Simpson (*22*). Dissolved sulfide was measured colorimetically according to Cline (*23*).

Waters for dissolved metals analyses were filtered using an acid-washed plastic syringe and 0.45 µm membrane filters (Minisart, Sartorius), acid-washed on-line before use. Filter blanks were prepared from Milli-Q water. Filtered waters were acidified by the addition of 5 mL/L concentrated HNO_3 (Trace Pur, Merck). Dissolved metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES)

(Spectroflame EOP, Spectro Analytical Instruments) calibrated with matrix-matched standards (QCD Analysts).

Three strengths of acid digestion were utilized for sediment-bound metals. Total particulate metals (TPM) were determined using an aqua regia digestion method (*20*). Simultaneously-extracted metals (analogous to the SEM fraction determined with AVS/SEM analyses), were determined by shaking wet sediment in 1 M HCl for 30 min, followed by sample filtration. Acid-soluble metals (ASM) were determined by shaking wet sediment in 0.2% HNO_3 for 5 min, followed by sample filtration. All extracts were analyzed by ICP-AES.

Surface sediment sampling and analyses. Five Dock Bay in Sydney Harbour, NSW, Australia, is a shallow, inter-tidal bay having 1.2 m tides that expose sediments within 20 m of the shoreline. Overlying waters are saline, warm and well oxygenated. Sampling and measurements of Bay sediments were conducted on three occasions in late summer 2001, at low tide (0.2-1.0 m water depths), at a series of sites within 20 m of the high water mark. Measurements of salinity, temperature, dissolved oxygen, and pH were made on the overlying water and pH and redox potential were measured in the 0-2 cm surface sediment layer.

Surface sediment samples were collected at low tide using a shovel to retrieve a large volume from depths of 20-40 cm of water, without disturbing the surface layer of sediment. A clean plastic spoon was used to transfer the top 0-2 cm of the collected sample to a clean 50-mL centrifuge tube. Centrifuge tubes were completely filled with sediment (no air bubbles or head space), capped, and placed on ice until returning to the laboratory.

Porewaters were extracted from surface sediments (0-2 cm depth) within 4 h of collection using the procedure described by Simpson et al. (*24*). In this procedure, sediment samples were centrifuged under a nitrogen atmosphere followed by 0.45 µm membrane filtration of the displaced porewater. Samples were taken for analysis of porewater metals,

dissolved sulfide and pH. The sediment remaining was frozen for later analyses of acid-extractable metals, acid-volatile sulfide (AVS), organic carbon and grain size.

Corer-reactor experiments and metal flux measurements. Ten sediment cores (15 cm depth) were collected at the site which had the highest porewater zinc concentrations, for metal flux measurements. Polycarbonate corer-reactor tubes (40 cm long, 15 cm diameter) were inserted to a depth of 15 cm into water-covered sediment (*19*). Valve closure at the top of the tube created a sufficient pressure seal to allow the corer-reactor to be removed intact with overlying water. Full tubes were capped at both ends and transported in an upright position to the laboratory.

In the laboratory, sediment corer-reactors were stored upright in a controlled-temperature environment (20±2ºC), similar conditions to that in which they were collected. The overlying waters of the sediments were stirred (30 rpm) and bubbled with air, maintaining a stable pH (7.8-8.0) and dissolved oxygen concentration (6-8 mg/L). The pH and dissolved oxygen concentrations of the overlying waters were monitored daily. The renewal of overlying water was achieved using a peristaltic pump to carefully drain and replace the 4 L of water with clean seawater (avoiding disturbance to the surficial layer).

For 'normal' operating conditions, the waters overlying the sediment cores were changed at the start of the week and overlying water samples taken (daily) in duplicate (filtered 0.45 μm). Samples taken during the course of experiments removed less then 5% of the original overlying water. These experiments were undertaken to determine the flux of metals from the sediments at similar pH and DO (dissolved oxygen concentration) as encountered naturally in Five Dock Bay. In the absence of capping materials, zinc fluxes were calculated from the difference between dissolved zinc concentrations measured 5 min and 4 h after water renewal and assuming a sediment surface area of 0.0177 m^2. Over this 4 h period, the rate of zinc

release from the sediments was usually constant, after which time the release rate often decreased as zinc concentrations increased the in overlying waters.

The effect of bioturbating/bio-irrigating organisms on metal fluxes was investigated using sediments which were effectively devoid of native organisms because of previous anoxic conditions. The anoxic conditions were created by replacing the overlying water with deoxygenated seawater (weekly) and bubbling the waters with nitrogen gas for two weeks (dissolved oxygen <0.1 mg/L). During this period, surfacing dead organisms were removed with minor disturbance. In the third week, conditions were returned to normal (for two weeks). Following this, five polychaete worms (*Australoneries ehlersi*) and five bivalves (*Soletellina alba*) collected from the estuarine Woronora River (NSW, Australia) were added to these sediment cores and overlying waters were sampled and replaced as for normal conditions. This density of organisms compared favorably with the density of these species at their collection site (unpublished results).

To investigate the effect that tides may have on zinc fluxes, four sediment cores, which had previously recorded near-constant (week-by-week) zinc fluxes, were subjected to daily rather than weekly renewal of overlying water. Although tides have a 12-h cycle, changing the waters on a shorter cycle was not practical for this study and a 24-h cycle was used. To simulate tides during the daily water renewal, the sediments were exposed to the atmosphere for 2 h before being refilled with fresh seawater. For two of these cores, organisms had previously been removed by a period of anoxia (as described above). When oxic conditions returned, fluxes stabilized during weekly water exchanges. For these experiments, overlying water samples were taken at times of 0, 1, 2, 3, 4, 6, 16 and 24 h following water replacement (simulating the incoming tide).

Capping materials tested for the containment of metal contaminants in the estuarine sediments of Five Dock Bay comprised (i) clean sand (20 mm), (ii) clean sediment (5 mm),

(iii) zeolite powder mixed 1:3 with clean sand (10 mm) and (iv) granular zeolite mixed 1:1 with clean sand (10 mm). Clean sand (grain size 99.3% >180 µm) was purchased from a local supplier. Clean sediment (for capping material) was collected from Grays Point, NSW, Australia and had a grain size of 89.3% >180 µm, 5% <63 µm. Natural zeolite (clinoptilolite) was from the Escott property, Werris Creek, NSW, Australia (Zeolite Australia Pty Ltd). Granular (100% particles 0.25-2 mm) and powdered (100% <63 µm) zeolite materials were tested. The experiments were performed in the corer-reactors, with capping materials carefully added to the surface of the sediments, taking care to avoid sediment resuspension, before renewal of overlying water. Experiments were performed with sand and sediment capping materials using (i) sediment cores containing native organisms, and (ii) with sediment cores for which organisms had been removed (through anoxia). Overlying waters were sampled daily for up to seven weeks and there was no renewal of overlying waters, but volumes were kept constant by small additions of clean seawater.

Results and Discussion

Sediment properties. Five Dock Bay is a severely metal-contaminated site, largely as a result of historical discharges from a wire-making plant. The surface sediments comprised silty sand, with typically 15-30% being <63 µm in size. Organic carbon concentrations ranged from 2 to 6%, although in areas where seagrass was present, concentrations were as high as 30%. Porewater pH ranged from 7.1 to 7.8 and redox potentials from -100 to 250 mV. Zinc and lead, and to a lesser extent copper, were the major metal contaminants in the sediments with total particulate and dilute-acid-soluble zinc (0.2% HNO_3) concentrations spanning 500-7000 µg/g and 100-1500 µg/g respectively (Table 1). These high metal concentrations extend to sediment depths of greater than 50 cm (unpublished results). Background concentrations of zinc, lead and copper in Sydney Harbour sediments have been

previously estimated at 47, 33, and 10 µg/g respectively using a 3:1 HNO_3:$HClO_4$ sediment digestion (*25*). The overlying waters had dissolved oxygen concentrations in the range 5-7 mg/L, temperatures 20-25ºC, and salinity 28-34‰.

In evaluating the quality of sediments with respect to heavy metal contaminants, the molar excess of acid volatile sulfide (AVS) (mainly FeS) over simultaneously-extracted metals (SEM), has been invoked to predict the absence of metal bioavailability and toxicity to benthic organisms (*26, 27*). In the surface sediments (0-2 cm), AVS and acid-soluble zinc (SEM, 1 M HCl) concentrations ranged from 0 to 30 µmol/g and 5 to 100 respectively. At all sites, surface sediment SEM concentrations exceeded AVS concentrations by between 5 and 75 µmol/g. According to AVS/SEM theory, porewater zinc concentrations may therefore be expected to be significant and have the potential to be bioavailable. Based on AVS/SEM analyses, the copper and lead in the sediments were not likely to be bioavailable. At depths greater than 2 cm, AVS concentrations exceeded acid-extractable (1 M HCl) zinc concentration and porewater zinc concentrations were low, <3 µg/L (unpublished results).

High porewater iron (100-4000 µg/L) and manganese (70-800 µg/L) concentrations were measured at most sites which, together with the measured redox potentials, indicated that predominantly sub-oxic conditions existed in the surface sediments. Disturbances to the sediments during collection was expected to cause speciation changes, including oxidation of porewater iron(II) by reaction with dissolved oxygen and manganese oxide phases and losses of dissolved metals by adsorption to fresh iron hydroxide precipitates (*17*). In the undisturbed sediments, the porewater iron and zinc concentrations may have been significantly greater (*17*). Porewater zinc concentrations (20-1200 µg/L) were above the water quality guideline value of 15 µg/L (*1*). The concentrations of other porewater metals were below water quality guideline values (e.g. <1.4 µg Cu/L, <4.4 µg Pb/L, <5.5 µg Cd/L). The porewater pH of the

surface sediments ranged from 7.1 to 7.8. Porewater sulfide was less than 1 μg/L in the surface-sediments.

For the surface sediment samples collected from the ten sites, porewater zinc concentrations were correlated ($r = 0.930$, $p<0.001$) with the molar excess of SEM-Zn (1 M HCl) over AVS (i.e. SEM-Zn - AVS). This was somewhat surprising given the oxic to sub-oxic nature of these sediments, and may indicate that either (i) the bioturbation has caused mixing of surface sediments with those from greater depths, or (ii) at some stage the surface sediments are sufficiently anoxic for sulfide formation (sulfate reduction by bacteria). Porewater zinc concentrations were not correlated with any of the acid-extractable zinc concentrations, aqua regia ($r = 0.51$, $p>0.1$), 1 M HCl ($r = 0.24$, $p>0.5$), 0.2% HNO_3 ($r = -0.49$, $p>0.1$) or with AVS ($r = -0.38$, $p>0.25$). This indicated that none of these extractions, alone, would be useful for predicting zinc partitioning to porewaters.

For the sampled sediments, a high variability was observed in the measured porewater iron, manganese and zinc concentrations, even for porewaters extracted from sediment samples collected at the same time from the same site and within 5-cm proximity. For example, at one site where the sediment cores were collected during the three sampling occasions, zinc concentrations ranged from 167 to 302, 49 to 251 and 365 to 1200 μg/L. Despite this variability for all sediment samples, porewater zinc concentrations were inversely correlated with the log of porewater iron ($r = -0.959$, $p<0.001$) and the log of manganese ($r = -0.889$, $p<0.001$) concentrations.

Previous studies have highlighted the dynamic nature of iron(II)-rich sediment porewaters in estuarine systems (*17*). Porewater iron and manganese concentrations are very redox sensitive and even small amounts of disturbance during sampling, through changes to dissolved oxygen concentrations or the intermixing of previously redox-stratified sediments,

will result in large changes to metal partitioning. Because zinc is rapidly adsorbed by iron (III) hydroxide, sediment disturbances which cause the oxidative precipitation of Fe(II) as $Fe(OH)_3$ and will result in lower porewater zinc concentrations (*17*).

Factors affecting zinc fluxes from sediments. In the absence of biological activity (e.g. bioturbation and bioirrigation) and physical forces (*e.g.* wave and current effects), Fick's first law of diffusion can be used to calculate the flux (J) of metals from the sediment to the overlying waters.

$$J = -F.D_{(sed)}.dC/dx$$

The measured porosity (F) of the sediments ranged from 55 to 80, and the sediment diffusion coefficient for zinc ($D_{(sed)} = 5.93\times10^{-10}$ m^2/s) was taken from Boudreau (*28*). The concentration gradient (dC/dx) was determined from the porewater concentrations (C) of the surficial sediments at a depth (x) of 1 cm and an overlying water zinc concentration of 20 µg/L (average measured, unpublished results). Based on these calculations, a maximum flux of zinc from the sediments of 5 mg Zn /m^2/day was estimated, using a porewater zinc concentration of 1200 µg/L and sediment porosity of 80. These calculations may, however, be a poor estimate of the true zinc flux as they are based solely upon the diffusion processes. They are also totally dependent on the ability to accurately sample (and analyse) the porewaters in the uppermost sediment layer, which is in itself a challenge (*17*). If the porewater zinc concentration in the top 1 mm of sediment was 1200 µg/L, then a maximum flux of 50 mg Zn /m^2/day would be estimated. Previous studies have found up to an order of magnitude difference between the calculated diffusional flux and the actual flux (*6, 29*).

For all sediment cores, the measured zinc release was rapid, and, within 4-5 h, zinc concentrations in the overlying waters became high enough to effect subsequent zinc release (as illustrated by the curvature in Figure 1). For repeat water changes, immediately following

water renewal the zinc fluxes remained high, indicating that the curvature was not due to a depletion of easily-released zinc. Using the zinc concentrations measured in the overlying waters 4-h after the water renewal on the day following collection, zinc fluxes for the ten cores were calculated to range from 10 to 89 mg Zn /m^2/day. These fluxes were greater, by up to an order of magnitude, than those calculated using Fick's first law of diffusion.

Simulated-tide experiments. In Table 2, the results from the simulated-tide experiments are compared with zinc fluxes measured from the same sediment cores for the 3-4 week period prior (with weekly water renewal). Although, zinc fluxes were calculated using the dissolved zinc concentrations 4-h following water renewal for both the daily and weekly water change experiments, zinc fluxes (from the same core) were greater following daily water changes than for weekly water changes. These experiments indicate that more frequent short periods of air-exposure followed by renewal of overlying water would result in a large increase in the zinc flux from these sediments. The zinc release did not appear to occur as a pulse, but rather a steady flux for the first 4 h after water renewal (as for Figure 1), but higher than that observed when overlying waters were exchange less frequently. The increased zinc flux for the tidal experiments (daily water change) may indicate that either (i) dissolved zinc concentrations increase in the surface sediments, or (ii) bio-irrigation induced zinc release increased due to increased organism activity immediately after waters were replaced.

The oxidation of sediments caused by exposure to oxygenated waters is well recognized as a process that increases dissolved metal concentrations in sediment porewaters (*8, 9, 17*). A greater increase in zinc flux was observed for the sediments that contained organisms than those for which organisms had been removed. This observation indicated that bio-irrigation may have an important role in controlling zinc fluxes, particularly after water renewal (incoming tides). Previous studies have shown that when sediments are exposed to the

atmosphere (i.e. tides are out), bio-irrigation ceases for many organisms, and when waters return, irrigation rates are initially high in order to renew burrow waters with fresh oxygenated waters (*13*). The effect of bioturbation has generally been to increase metal fluxes from sediments, however the magnitude of the effect is also dependent on organism type and physico-chemical conditions such as dissolved oxygen and tides (*5, 8*).

Effect of organisms. To assess the effect of macroscopic organisms on zinc fluxes, measurements were made on six sediment cores with and without sediment-dwelling organisms present (Table 3). Zinc fluxes were initially measured for 3 weeks with native organisms present, then the sediment cores were made anoxic for two weeks (to kill the native organisms) and following another two weeks recovery (under oxic conditions) zinc fluxes were measured for three weeks (no organisms).

Increased zinc fluxes were usually observed for sediment cores that contained organisms than for the same cores with no organisms, consistent with many previous studies (*5, 8*). It cannot be discounted that the process of organism-removal (the anoxia) also affected the zinc fluxes, however little disturbance to the sediment occurred during this process and the 'recovery time' following the period of anoxia appeared sufficient for zinc fluxes to stabilize. The effect of the period of anoxia on microbial populations, and their effect on zinc fluxes, is also unknown. In the presence of organisms, high amounts of suspended solids (105±24 mg/L) were apparent in the waters above the sediments. In the absence of organisms, the waters were much clearer, with suspended solid concentrations being lower (30±5 mg/L). These experiments showed that bioturbation and bio-irrigation actions of organisms significantly increase zinc fluxes from the sediments. This could present major problems with capping materials.

The effect of bioturbation by recolonizing organisms on zinc fluxes from sediments previously devoid of organisms was demonstrated by the addition of five bivalves, *Soletellina*

alba and five worms, *Australoneries ehlersi* to the sediment corer-reactors from which native organisms had previously been removed (Table 4). For the three weeks following the addition of the new organisms, zinc release rates were much lower than those observed before organism addition. Previous studies have also observed that the effect of organisms is greatest immediately after introduction to sediments (*8*). The observed lower zinc fluxes can be attributed to iron(II) oxidation and adsorption of porewater zinc to freshly precipitated iron(III) hydroxide phases as a result of sediment disturbances by the initially highly active organisms. When the organisms appeared to have established themselves in the sediments, as indicated by them moving around less, the zinc fluxes increased again and became greater than the release rates measured in the absence of organisms (Table 3). The recovery of greater than 70% of the organisms at the end of each experiment indicated that organism mortality was low. The disturbances to metal partitioning in iron(II)-rich sediments caused by sediment-dwelling organisms has been discussed elsewhere (*17*). The observations are consistent with past studies showing significant changes to porewater iron(II) concentrations due to sediment-dwelling organisms (*12-14*).

Sediment capping. The effectiveness of capping materials in reducing the flux of zinc from the metal contaminated estuarine sediments of Five Dock Bay was determined by comparing fluxes from sediments overlain with capping materials to the fluxes before the capping materials were installed. The grain size distributions of the materials used were (i) 89.3% >180 μm, 5% <63 μm (sediment), (ii) 99.3% >180 μm (sand), (iii) 100% <63 μm (zeolite powder) and (iv) 100% 0.25-2 mm (granular zeolite). The exchange capacity of the zeolite powder was 1.19 meq/g. The capacity of the sediment to adsorb metal ions was not determined but was expected to be greater than that of the zeolite and also less affected by external conditions due to the large number of different binding sites.

Figure 2 shows the mean releases of zinc from sediments capped with sand, zeolite/sand mixtures and clean sediment for a 42-day period. The calculated fluxes for the different capping experiments are summarized in Table 5. Following the application of capping materials to sediments containing no animals, zinc fluxes were reduced to ~0.01 (5 mm sediment), ~0.24 (15 mm zeolite/sand mixtures), and ~0.54 mg/m^2/day (20 mm sand) compared to >30 mg/m^2/day for uncapped sediments.

The clean sediment cap was the most effective in reducing the zinc flux. The effectiveness of the barrier materials will be related to their ability to physically isolate the contaminated sediments from the overlying water and their adsorption properties for released zinc. Based on diffusion, the breakthrough of zinc from the deeper sediments through the 5 mm clean sediment barrier would be expected to occur within 48 h (*30*). The observation of no break-through of zinc after 42 days indicate that the clean sediment cap prevented zinc fluxes not just by physical isolation. Zeolite-powder mixed 1:3 with clean sand (10 mm) and granular zeolite mixed 1:1 with clean sand (10 mm) showed little difference in their ability to reduce zinc fluxes (Figure 3).

The presence of native benthic organisms severely restricted the ability of the sediment (5 mm) and sand (20 mm) as capping materials to reduce the flux of zinc from the sediments (Figure 4). For sediments capped with clean sediment (5 mm), the presence of organisms resulted in a rapid release of zinc during the first day (5.7 mg/m^2/day), after which period zinc fluxes were ~0.3 mg/m^2/day. Similarly, for sediments capped with sand, the presence of organisms resulted in a rapid release of zinc during the first day (9.8 mg/m^2/day), after which period zinc fluxes were ~3.5 mg/m^2/day.

Function of Capping Materials. Before the addition of the capping materials, the top 5 mm of the surface sediments was a light brown colour, probably indicating the presence of iron (hydr)oxides. Following the addition of the capping materials however, the sediments

below the capping materials slowly changed to a dark brown-black colour, consistent with the establishment of anoxic conditions and the formation of sulfide phases within these sediments (i.e. FeS). On the removal of the clean sediment capping material (no organisms), the zinc flux was slow to return to a level similar to that measured before the application of the barrier. For this sediment, the original zinc flux was 59±5 $mg/m^2/d$, <1 $mg/m^2/day$ with a sediment barrier, and 16, 25, 32, 42 and 56 $mg/m^2/day$ for the five weeks following barrier removal. It is likely that the flux during the first week following the barrier removal was low due to sediment disturbances that occurred during the removal of the barrier. For the four subsequent weeks, however, the increasing fluxes were most likely associated with the slow oxidation of zinc sulfide phases upon exposure to the aerated waters. Previous studies have shown that zinc sulfide oxidation occurs slowly over days (*31*) and that increased dissolved oxygen concentrations in waters overlying sediments will increase metal fluxes (*8, 9, 17*).

These observations indicated that for metal-contaminated sediments, metal-sulfide formation, due to anoxia below capping materials, is an important function of sediment capping for limiting fluxes of metal-sulfide-forming metals (e.g. Cd, Cu, Hg, Ni, Pb, Zn). Clean sediments offer significant advantages over most other materials as effective capping materials for metal-contaminated sediments in estuarine environments. Although poorly characterized, silty sediments have extremely high adsorption capacities for most trace metal ions. The high density and diversity of metal-ion binding sites of natural sediments (dominated by iron hydroxy, carbonate and organic substrates) ensures high binding capacities under a wide range of conditions. Importantly, natural sediments offer the most suitable substrate for re-colonization by organisms and the establishment of a healthy ecosystem compared to ‘foreign’ materials such as zeolites. There is also likely to be a cost advantage in using natural sediments.

All capping materials will be expected to be heavily bioturbated by organisms, and this will reduce the ability of capping materials to decrease the contaminant fluxes from the sediments. On the basis of our findings, any capping should be applied to a depth greater than that to which most native organisms burrow, i.e. at least >30 cm, so as to effectively isolate the underlying contaminated sediments from the bioturbating activities of the benthic organisms. For such depths, only natural materials would be acceptable, otherwise the natural ecosystem would be effectively smothered and unlikely to readily recolonize.

For shallow bays like Five Dock Bay, the addition of a capping material to such a depth, without first removing sediment, would alter the sediment topography and result in the increased exposure of the sediments to the atmosphere during tidal cycles. The deposition of a capping material close to the water surface also exposes the capping material to greater erosional forces such as wave and wind action and possible boat scouring. Consequently, it would be recommended that for shallow-water sediments, some of the contaminated surficial sediments be removed (dredged) prior to capping to minimize these effects.

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Tables

Table 1. Metals in surficial sediments from Five Dock Bay

Extraction Method	Cd	Cr	Cu	Ni	Pb	Zn	Mn	Fe
				µg/g				%
Aqua regia (24 h)	1-3[1]	15-70	40-150	5-20	80-700	500-7000	50-150	1-3
1 M HCl (30 min)	0.5-2	5-25	20-70	1-4	50-400	400-6000	10-40	0.2-0.8
0.2% HNO_3 (5 min)	<0.5	1-5.5	0.5-6	0.5-2	10-60	100-1500	4-20	0.05-0.2
Sediment quality guideline[2]	1.5	80	65	21	50	200	-	-

[1] Ranges given are for measurements on twenty sediment samples.

[2] ANZECC/ARMCANZ (2000)

Table 2. A comparison of zinc flux rates for sediments exposed to weekly or daily tides (water renewal).

	Zinc flux, $mg/m^2/day$ [1]	
Core type	Weekly water renewal [2]	Daily water renewal [3]
Native organisms	14±7	63±14
Native organisms	17±20	92±12
No organisms	14±3	29±12
No organisms	30±6	48±14

[1] Calculated using dissolved zinc concentrations 4-h following water renewal.

[2] Mean ± two standard deviations for three water renewals (3 weeks data).

[3] Mean ± two standard deviations for eight water renewals (2 weeks data)

Table 3. Zinc fluxes in the presence and absence of organisms.

	Zinc flux, $mg/m^2/day$ [1]	
Sediment	Organisms present	No organisms
Core 3	95±18	28±6
Core 4	95±19	29±6
Core 5	48±10	31±6
Core 6	50±10	27±5
Core 7	32±6	14±3
Core 8	26±5	30±6

[1] Calculated using dissolved zinc concentrations 4-h following water renewal.
Results are mean ± two standard deviations for three water renewals (3 weeks data).

Table 4. Zinc fluxes from two sediment cores following addition of sediment-dwelling organisms.

	Zinc flux, $mg/m^2/day$ [1]	
	Core 5	Core 6
No organisms	31±6 [2]	27±5 [2]
Added organisms, week 1	15	18
Added organisms, week 2	16	11
Added organisms, week 3	36	41
Added organisms, week 4	27	34
Added organisms, week 5	43	71

[1] Calculated using dissolved zinc concentrations 4-h following water renewal.
[2] Results are mean ± two standard deviations for three water renewals (3 weeks data).

Table 5. Zinc fluxes from sediments following the application of capping materials.

	Zinc flux, $mg/m^2/day$ [1]			
Capping material	Original	0-24 h	2-5 days	6-25 days
Sediment, no animals	19	0.36	0.006	<0.001
Sediment, animals	14	5.7	0.23	0.36
Sand, no animals	12	0.15	0.64	0.51
Sand, animals	80	9.8	3.7	3.4
Zeolite, no animals	30	0.72	0.19	0.23
Zeolite powder, no animals	31	0.84	0.28	0.14

Figure Captions

Figure 1. Release of zinc in 24 h corer-reactor experiments from sediment cores 1 (∗), 2 (△), 7 (◆) and 8 (○) collected from Five Dock Bay, Sydney. Data represented as are mean ± three standard deviations (error bar) of dissolved zinc measurements on each cores.

Figure 2. Mean release of zinc in corer-reactors from sediments capped with sand (20 mm), zeolite/sand mixtures (10 mm) and clean sediment (5 mm) for a 42 day period (no organisms present). Data represented as are mean ± standard deviation (error bar) of measurements on replicate core treatments.

Figure 3. Release of zinc in corer-reactors from sediments capped with zeolite/sand mixtures (10 mm) (a) 25% zeolite powder (dashed line) and (b) 50% granular zeolite (solid line).

Figure 4. Release of zinc in corer-reactors from sediments capped with sediment (5 mm) or sand (20 mm) with and without the presence of native organisms.

Figure 1

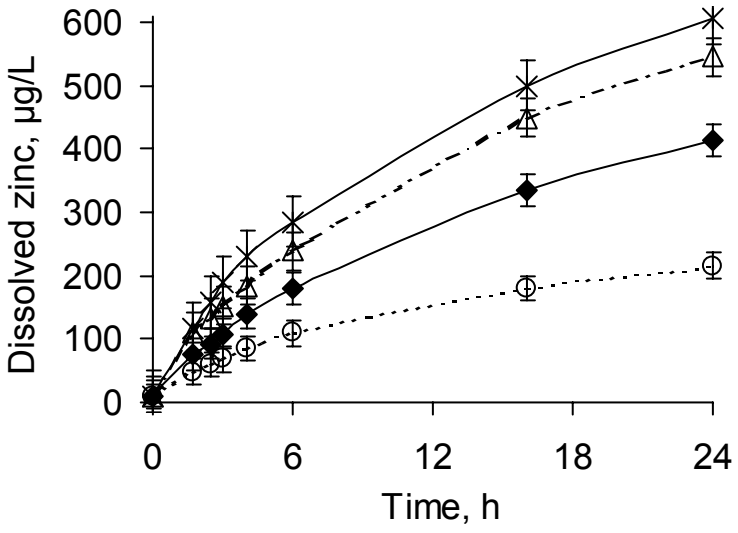

Figure 2

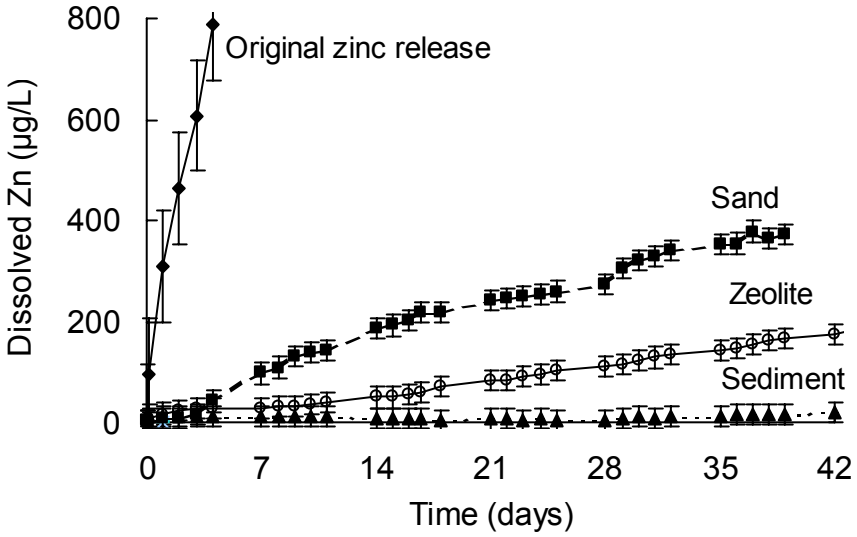

Figure 3

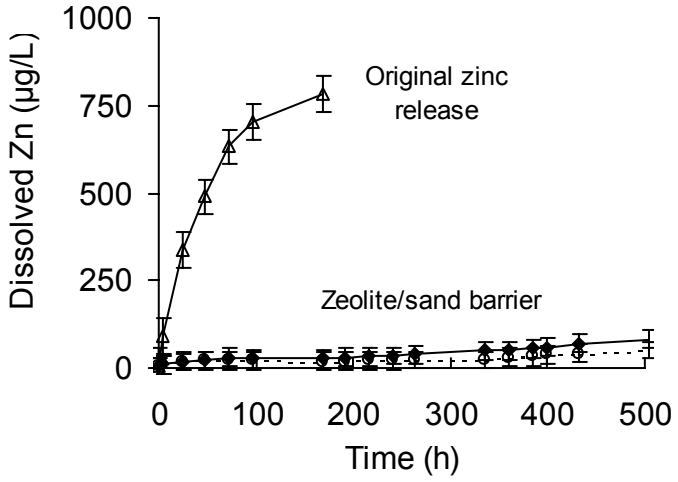
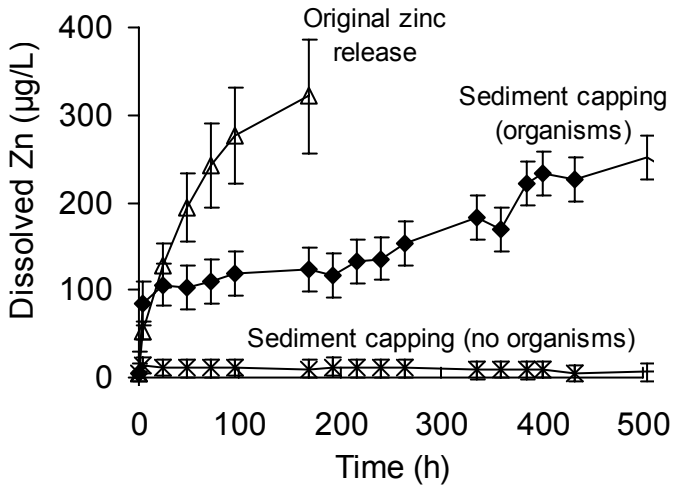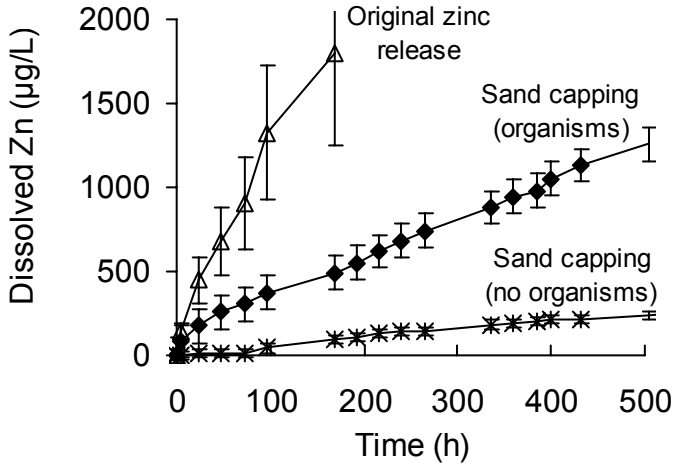
Figure 4