Processes controlling metal transport and retention as metal-contaminated groundwaters efflux through estuarine sediments

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Abstract
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Processes controlling metal transport and retention as metal-contaminated groundwaters efflux through estuarine sediments.

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Factors affecting the transport and retention of Cd, Cr, Cu, Ni, Pb and Zn in acidic groundwaters as they pass through estuarine sediments were investigated using column experiments. Acidic groundwaters caused the rapid dissolution of iron sulfide (AVS) and other iron and manganese phases from sediments that are important for metal binding and buffering. Metal breakthrough to overlying water occurred in the order of Ni>Zn>Cd>>Cu>>Cr/Pb. Metal transport increased as the sediment permeability increased, reflecting the low resistance to flow caused by larger sand-sized particles and the decreased abundance of metal adsorption sites on these materials. Metal mobility increased as the groundwater pH decreased, as flow rate or metal concentrations increased, and as the exposure duration increased. Groundwater Cr and Pb were promptly attenuated by the sediments, the mobility of Cu was low and decreased rapidly as sediment pH increased above 4.5, while Cd, Ni and Zn were the most easily transported to the surface sediments and released to the overlying waters. For groundwaters of pH 3, metal migration velocities through sandy sediments were generally 0.5-2% (Cr, Pb), 1-6% (Cu) and 4-13% (Cd, Ni, Zn) of the total groundwater velocity (9-700 m/year). The oxidative precipitation of Fe(II) and Mn(II) in the groundwaters did not affect metal mobility through the sediments. The results indicated that the efflux of acidic and metal-contaminated groundwater through estuarine sediments would affect organisms resident in sandy sediments more greatly than organisms resident in fine-grained, silty, sediments.

Key Words— Groundwater, Metals, Transport, Retention, Sediment
1 Introduction

The efflux of acidic and metal-contaminated groundwater through surface sediments may threaten the integrity of many productive estuarine environments. In Sydney Harbour, Australia, metal contaminated groundwater represents a challenge for sediment quality assessments in estuarine bays adjacent to industrial land. Metal contaminants of concern include chromium leaching from land in-filled with industrial waste, mercury near naval dock yards, and zinc from steel galvanising operations. Groundwater contaminants accumulated in surface sediments are a risk to many sediment-dwelling organisms that ingest sediment and detritus material (Wang and Fisher, 1999). Submarine groundwater discharges may increase the flux of metals from contaminated sediments to overlying waters and the exposure of contaminants to filter-feeding organisms and plants.

To date, the majority of the process-related research into groundwater contaminants has been concerned with contaminant-leaching from landfills and the transport processes of these contaminants in aquifers (Christensen et al., 2001). Few studies have investigated the processes controlling the transport of contaminants in groundwater at the interface between subsurface groundwater and saline marine waters (Li et al., 1999; Uchiyama et al, 2000; Lui et al., 2001; Charette and Sholkovitz, 2002; Zhang et al., 2002). Heavy metals do not frequently constitute a problem in landfill groundwater plumes because leachates usually contain only modest concentrations of heavy metals and these are strongly attenuated by sorption or precipitation reactions (Christensen et al., 2001). However, in land areas that have received waste from metal industries, groundwater metal concentrations can become very high (1-100 mg/L range). Little is known about the effect of acidic, metal-contaminated groundwater on estuarine sediments through which groundwater may emerge in coastal regions.

This study investigates the mobility and retention of Cd, Cr, Cu, Ni, Pb and Zn in acidic groundwater as it passes through estuarine sediments. Sediment columns that enabled groundwater to be introduced at their base and flow up through the sediments, were used to characterise changes to the mobility of metals due to changes in sediment permeability, groundwater flow rate, pH, metal concentration, and the presence of Fe(II) and Mn(II). Experiments also investigated the effect of acidic groundwater on the important metal binding phase, iron monosulfide (acid-volatile sulfide, AVS).

The results are discussed in terms of the mobility of metal contaminants and possible impacts to benthic organisms that inhabit estuarine sediments through which groundwaters efflux in coastal environments.
2 Materials and methods

All glass and plasticware was cleaned by soaking in 10% (v/v) HNO$_3$ (Trace Pur, Merck) for >24 h followed by rinsing with deionised water (Milli-Q, Millipore). All laboratory-ware used for dissolved metals sampling and analysis was cleaned in a Class-100 laminar-flow cabinet (metal-free HWS, Clyde-Apac). All chemicals were analytical reagent grade or equivalent analytical purity. Deoxygenated solutions were prepared by bubbling solutions with oxygen-free nitrogen gas for >8 h to give dissolved oxygen concentrations <0.1 mg/L. These solutions were stored in a nitrogen gas-filled glove box.

Measurements of pH (calibrated against pH 4 and 7 buffers) were made as described previously (Simpson and Batley, 2003). All water filtrations were made using a plastic syringe and plastic encaptulated 0.45 µm cellulose nitrate membrane filters (25 mm, Minisart, Sartorius) that were acid-washed with 20 mL of 2% HNO$_3$ (Trace Pur, Merck) and rinsed with 40 mL of deionised water before use. Dissolved metal concentrations were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Spectroflame EOP, Spectro Analytical Instruments) calibrated with matrix-matched standards according to Simpson et al. (2002). High-purity Milli-Q deionised water (18 MΩ/cm) was used to dilute analysis solutions.

Clean seawater was collected from Cronulla, NSW, Australia. Sediments were collected from Gray's Point (GP), Port Hacking estuary, Sydney, Australia. Roots and debris (wood, shells) were removed from the sediment by sieving through a 5 mm nylon sieve and sediments were stored in the dark at 4°C for a maximum of 60 days before use. Sand that was used for mixing with sediments was Sydney Sand, purchased locally.

Sediment porosity, wet density, and moisture content were determined according to standard methods (Mudroch et al., 1997). Sediment size fractionation determinations have been described previously (Simpson et al., 1998). Acid-volatile sulfide (AVS) was determined according to Simpson (2001). Acid-extractable metals were determined by addition of 20.0 mL of 1 M HCl to 0.400 g of wet sediment, briefly shaking and analysis of filterable metals (by ICP-AES) after 24 h extraction.

The sediment pH and acid-neutralising capacity (ANC) were measured on a mixture of 2.00 g wet sediment and 2.00 g deoxygenated Milli-Q water. pH measurements were made five minutes after mixing in a nitrogen filled glove box. ANC measurements were made by measuring the pH 24 h after the addition of 2.00 mL of 0.001 M HCl (pH 3) to the Milli-Q wetted sediment. The ANC was calculated as, \( \text{ANC} = 0.001 - 10^{(\text{pH})} \) (in µmol/g dry weight). Duplicate analyses and measurements were performed on 10% of all samples.
2.1 Artificial groundwater compositions

Artificial groundwater solutions were prepared by dilution of 1000 mg/L metal stock solutions with deoxygenated Milli-Q water containing 25 mg/L MgSO₄·7H₂O and 50 mg/L of CaCl₂·2H₂O. Chloride salts were used for Cd, Cr, Cu, Fe and Mn, sulfate salts for Ni and Zn and a nitrate salt for Pb. Groundwater solutions were acidified to pH 3, 4 or 5 using concentrated HCl and stored in a nitrogen gas-filled glove box.

2.2 Column experiments

Single- and 4-column experiments were designed to investigate the interaction of the artificial, acidic, metal-contaminated groundwater with sediments during the passage of groundwater vertically upwards through sediment-filled columns.

Four-column experiments consisted of four small polycarbonate tubes (35 mm diameter, 600 mm length) positioned tightly within a wider Perspex tube (92 mm diameter, 500 mm length) (Figure 1). Silicon sealant (Marine Silastic, Dow Corning) was used to fill all gaps between the tubes and fix the smaller tubes into position within the larger tube. A perforated Perspex retainer was secured in the centre of each tube 210 mm above the tube base. This ensured that the sediment in the tubes would not move upwards during the passage of the groundwater. Test sediments were added to the tubes while inverted. Mixtures of sediments and sand that had been saturated with seawater was added to each of the four smaller tubes to create a 200 mm column of sediment that extended from 10 mm above the base of the tubes to the Perspex retainer. Clean sand (saturated with seawater) was used to fill the bottom 10 mm of the small tubes and to create a 50 mm layer in the base of the wider tube. Groundwater inlet tubes were positioned in the middle of the 50 mm sand layer with the sand acting as a dispersive substrate for the groundwater solution. A Perspex base plate was attached to the base of wider tube with silicon sealant to create a watertight seal. Water entering through the inlet tubes passed through the sand and up through, but not around, any of the single columns within the 4-column system. Three identical 4-column systems were constructed for the simultaneous experiments.

Single-column experiments used the smaller tubes and same sediment packing procedures as the 4-column system. A rubber bung, fixed in place with silicon sealant, was used to seal the base of the single columns. Groundwater entered the base of the columns through a tube in the centre of the bung.
An airpump and fine tubing was used to bubble air into 20 cm of overlying water above the sediment columns to maintain circulation. The groundwater inlet tubes were connected to peristaltic pumps (Minipuls 3, Gilson) using 0.89 mm I.D. PCV pump tubing (A.I. Scientific, Australia).

2.3 **Sediment permeability and groundwater flow rate experiments**

Experiments investigating the effect of sediment permeability and flow rate on the transport of groundwater metals and acidification processes used the 4-column systems. The four columns contained sediments with different composition: 100% Gray’s Point (GP) sediment and mixtures of GP sediment and sand at ratios of 1:1, 1:2 and 1:3 (GP:sand). For three identical 4-column systems, groundwater of pH 3 and containing mixtures of Cd/Cr/Cu/Ni/Zn at 10/10/50/10/50 mg/L, respectively, was pumped into the base of the systems at flow rates of 9 (slow), 54 (medium) and 700 m/year (fast) (4.0, 24, 300 mL/h, respectively). The duration of the experiments was 773, 94 and 8 h for the slow, medium and fast flow rates experiments, respectively.

During the experiments the overlying waters in each of the twelve smaller columns were sampled regularly to monitor the breakthrough of groundwater metals from the sediments. 10-mL water samples were taken and filtered (0.45 µm) into 20 mL polyethylene vials. Samples were acidified to 1% acid with concentrated HNO₃ (Trace Pur, Merck) and metals analysed by ICP-AES. The total volume of water passing through each sediment column was measured and used to calculate the permeability of each sediment column.

At the end of the experiments, the sediment columns were frozen rapidly using dry-ice and stored upright in a freezer until time of sectioning. Cores were sectioned into 2 cm slices while still frozen and then thawed in a nitrogen gas-filled glove box before pH, ANC and acid-extractable metals analyses on each section.

2.4 **Groundwater flow duration, metal concentration and pH experiments**

Single-column systems were used to investigate the effects of flow time, metal concentration and pH on sediment acidification and metal transport processes. The sediment mixtures comprised 1:2 GP-sediment:sand and the groundwater flow rate was 80 m/year (9.0 mL/h). To investigate the effect of flow time, experiments were run for 24, 48, 96 and 168 h with groundwater of pH 3 and mixtures of Cd/Cr/Cu/Ni/Pb/Zn at 10/10/50/10/50/50 mg/L, respectively. The 96-h treatment was run in duplicate. To investigate the effect of pH, experiments were run for 168 h using groundwater of pH 3, 4 and 5 and metal mixtures of 5 mg/L Cd/Cr/Cu/Ni/Zn. The pH 4 experiment was run in duplicate.
To investigate the effect of metal concentration, experiments were run for 168 h using groundwater of pH 3 and metal mixtures of Cd/Cr/Cu/Ni/Pb/Zn at ‘high’ (10/10/50/10/50/50 mg/L, respectively), ‘medium’ (2/2/10/2/10/10 mg/L, respectively) and ‘low’ (0.4/0.4/2/0.4/2/2 mg/L, respectively) concentrations. The medium metal concentration experiment was run in duplicate. At the end of each experiment the cores were frozen, sectioned and analysed as described for the effect of sediment permeability and flow rate experiments.

2.5 Groundwater Fe(II) and Mn(II) experiments

Single-column systems were used to investigate the effect of groundwater Fe(II) and Mn(II) on metal transport. The sediment mixtures comprised 1:2 GP-sediment:sand and the groundwater flow rate was 80 m/year (9.0 mL/h). Experiments were run for 168 h using groundwater of pH 3 containing 2/2/10/2/10/10 mg/L Cd/Cr/Cu/Ni/Pb/Zn, respectively, and Fe(II)/Mn(II) at three different concentrations: (i) 0/0, (ii) 5/1, or (iii) 20/5 mg/L, respectively. At the end of the experiments the cores were treated and analysed as described for the effect of sediment permeability and flow rate experiments.

2.6 Effect of acidic groundwater on sediment sulfide phases

Single-column systems were used to investigate the effect of acidic groundwater on the acid-volatile sulfide (AVS) phases which are important for metal binding in sediments. A 1:2 GP-sediment:sand mixture was spiked with sufficient dissolved sulfide (Na₂S) to result in an AVS concentration of approximately 40 µmol/g and equilibrated for three weeks before use. Deoxygenated groundwater of pH 5 was pumped through the sulfide-spiked sediment columns at a rate of 9.0 mL/h for 2, 6 or 24 hours. AVS was analysed on sediment core sections at the completion of the experiments and compared with the AVS concentration measured before groundwater exposure.

3 Results and discussion

3.1 Sediment properties

The Gray’s Point (GP) sediment comprised 46% water, 4.5% organic carbon (dry weight) and had a particle size distribution: 11% <63 µm; 6% 63-180 µm; 64% 180-600 µm and 19% 600-1000 µm. The sediment pH was 7.3. The acid-extractable metal concentrations (in µg/g) were 1340 (Fe), 4.7 (Mn), 28 (Zn), 19 (Pb), 10 (Cu), 1.0 (Ni) and 0.3 (Cd) (Simpson et al., 2004). The sand that was mixed with the GP sediment comprised 100% 600-1000 µm sized particles and <0.1% organic carbon.
3.2 Effect of sediment permeability on groundwater flow rate and sediment acidification processes

The physical properties of the sand-sediment mixtures and the permeability of the sediment columns at different flow rates are shown in Table 1. The permeability of the sediments increased as the proportion of coarse-grained particles increased. Conversely, the sediments with the highest porosity (smallest grain size) were the most resistant to the simulated groundwater flow. This may be attributed to poor interconnectedness between pores and localised resistance to water movement between the small pores in the fine-grained sediments. As the total flow rate was increased from 9 to 700 m/year, there was a proportional increase in the flow going through coarse-grained sediments (columns 3 and 4), but not for the finer-grained sediments (columns 1 and 2).

The magnitude of natural groundwater flow rates can be quite varied, both between sites and between different flow paths within the same site. Tides, waves, storms, bioturbation and anthropogenic activities will all affect groundwater discharge rates in coastal environments. In near-shore aquifers, the upwards deflection of groundwater flows by salinity density gradients is expected to result in a greater flow rate in the upper portion of shoreline sediments than the mean groundwater flow rates throughout the aquifer (Lui et al., 2001). Submarine groundwater discharge rates have been reported as ranging from 0.01 to 2630 m/year (Lui et al., 2001). The current study indicated that high (500 m/year range) groundwater flow rates are only likely to occur in very sandy sediments and that most of the groundwater will flow around (not through) fine-grained (silty) sediments until coarse-grained (sandy) sediments are accessible for discharge to the overlying water environment. Consequently, silty sediments should receive a lower exposure to groundwater contaminants.

The passage of the pH 3 artificial groundwater through the sediments caused acidification of the sediments (Figure 2). The most permeable sediments (greatest proportion of sand) were the most acidified due the greater volume of groundwater that passed through these sediments. The deeper sediments, that were the first exposed to the groundwater, were more greatly acidified than the upper sediments, indicating that the groundwater was becoming less acidic as it passed through the sediments. The acid-neutralising capacity (ANC) of the sediments decreased with increasing exposure to the acidic groundwater (Figure 3). The loss of ANC relates to a dissolution of hydroxide and carbonate phases in the sediments (e.g. iron carbonate and hydroxides). For sediments of the same permeability, the sediment acidification and loss of ANC decreased with increasing groundwater flow rate (data not shown).
3.3 Effect of sediment and groundwater properties on metal transport through sediments

The water above the sediment columns was regularly sampled and analysed for dissolved metals throughout the experiments. In Figure 4, the ‘breakthrough’ of metals into the overlying water is shown. The order in which metal breakthrough occurred was Ni>Zn>Cd>>Cu>>Cr/Pb. For time periods greater than 24 h, the amount of Ni, Zn and Cd exiting the sediment column to the overlying water was greater than the amount of these metals entering in the groundwater at the column base. This indicated that although the transport of these metals in the groundwater had initially been attenuated by the sediment mixture (adsorbed or precipitated), the metals were released back into the groundwater after longer time periods. The release of Ni, Zn and Cd from the sediments may be attributed to the decrease in the sediment pH and the loss of binding phases (e.g. iron hydroxides) as the sediments became acidified due to prolonged exposure to the acidic groundwater (pH 3). For the total flow rates of 9, 54 and 700 m/year, breakthrough of Ni, Cd and Zn through the more sandy sediments (1:2 and 1:3 GP-sediment:sand) occurred after approximately 15, 1.5, and 0.07 days, respectively (data not shown). No breakthrough of metals was observed for the more silty (1:0 and 1:1 GP-sediment:sand) sediment mixtures during the time frame of the experiments.

The attenuation of groundwater metals by the sediments was characterised by measurements of the acid-extractable metals retained in the sediments at the completion of the experiments (Figures 5-8). The attenuation of metal transport through the sediment columns reflected the properties of the sediments, the groundwater flow rate, sediment acidification and the adsorption and solubility characteristics of the metals. The depth profiles for Cd, Ni and Zn retention in the sediment columns were very similar in shape. The profiles for Cr and Pb retention were very similar in shape.

The attenuation of metals in the groundwater (by the sediments) increased in the order Cd<Ni~Zn<<Cu<<Cr~Pb. Reactive sulfide (AVS) concentrations were low in the sediments and the mobility of metals in the sediments was expected to be controlled by the solubility of carbonate (solubility of MeCO$_3$($s$): Ni>Zn>Cu>Cd>>Pb) and hydroxide (solubility of Me(OH)$_2$($s$): Cd>Ni>Zn>>Cu>>Pb>>Cr(OH)$_3$($s$)) phases and adsorption onto iron hydroxide phases (Ni<Cd<<Zn<<Cu<<Pb<<Cr (strongest adsorption)) (Mineql, 1998).

The increased duration of exposure of the sediments to the acidic groundwater decreased the attenuation of Cr, Cu, Ni and Zn, but had little effect on the attenuation of Cr and Pb over the duration of the experiments (Figure 5). This pattern was consistent with the observed metal-breakthrough into the overlying waters (Figure 4). The high retention of Cr and Pb reflected the high particle reactivity of these metals and the decreased solubility of these metals as the groundwater pH increased during
the passage through the sediments (Figure 2). The decreased attenuation (increased migration) of Cd, Cu, Ni and Zn reflected the acidification of the deeper sediments and possibly the saturation of strong metal binding sites in the deeper sediments. Past studies have found that the pH at which ~50% of a metal is adsorbed to solid phases (the adsorption edge) occurs at pH 4.0 and 4.4 for Cr and Pb, respectively, near pH 5.2 for Cu, and at 6.0, 6.3 and 6.8 for Cd, Zn and Ni, respectively (Stumm and Morgan, 1996). This is consistent with the greater mobility of Cd, Ni and Zn as the acidity of the deeper sediments increased. During the 7-day period of groundwater flow, the Fe and Mn concentrations in the sediments decreased at a rate of 10±1 and 0.05±0.01 µg/g sediment /day, respectively. This indicated that iron and manganese phases (e.g. hydroxides) were being dissolved by the acidic groundwater and was consistent with the loss of ANC over this time period (Figure 4).

The attenuation of Cd, Cu, Ni and Zn decreased with increasing groundwater metal concentrations (Figure 6). In these experiments, the groundwater was initially pH 3 and the pH profiles in the sediments at the completion of the experiments (data not shown) were very similar for the three series of metal concentrations investigated. This indicated that the differences in metal attenuation were not due to difference in pH and that competition for metal binding sites on the sediment particles was the most likely cause of the decreased attenuation of these metals as groundwater metal concentrations increased. The attenuation of Cd, Ni and Zn were more affected than Cu was by increasing metal concentrations in the groundwater. This may be attributed to the stronger binding of Cu to sediments than occurs for Cd, Ni and Zn. Increased metal concentrations did not appear to affect the attenuation of Cr or Pb and was consistent with neutralisation of the groundwater controlling the solubility, and attenuation, of these metals.

The attenuation of the groundwater metals decreased with increasing groundwater flow rate (Figure 7). Very little Cd, Ni and Zn was retained in the 1:3 GP-sediment:sand mixture at the highest groundwater flow rate (1790 m/year, Table 1). At slower groundwater flow rates (18, 129 m/year), Cd, Ni and Zn were retained in the upper sediments, but not in the deeper sediments which had become acidified (Figure 7). At all flow rates, the movement of Cu was attenuated by the sediments, however a greater amount of Cu was retained by the sediments at the slower flow rates. The transport of Cr and Pb in the groundwaters was attenuated strongly by all sediment mixtures and at all flow rates. Chromium and Pb were only observed to move through the most permeable sediment mixture (1:3 GP-sediment:sand) at the highest flow rate.
Metal attenuation decreased as the permeability of the sediments increased (Figure 8) and reflected the decreased abundance of metal adsorption sites (greater proportion of sand) and the greater acidification of the more permeable sediments (Figure 2).

3.4 Metal migration velocities

The determination of metal migration velocities is useful for quantifying the transport of groundwater-derived metals through sediments. Metal migration velocities were calculated from the profiles of metals deposited in the sediments by dividing the depth (distance, m) at which 50% of the total deposited metal occurred (this usually corresponded with the position of the peak metal concentration following the subtraction of the background concentrations) by the groundwater flow duration (time, years).

In Table 2, the effect of sediment permeability on the migration velocities of Cd, Cr, Cu, Ni and Zn are shown for a groundwater flow rate of 9 m/year. In the most permeable sediment (1:3 GP sediment:sand mixture), the metal migration velocities, calculated as a percent of the groundwater flow rates, were 8.2%, 7.6%, 7.1%, 4.9% and 1.2% for Cd, Zn, Ni, Cu and Cr, respectively. The metal migration velocities increased by 0.2-2% (of the total groundwater flow rate) as the flow rate increased from 9 m/year to 700 m/year (Table 1).

Groundwater pH is expected to have a large effect on metal migration velocities (Christensen et al., 2001). The effect of groundwater pH on the migration velocity of Cd, Cr, Cu, Ni and Zn is shown in Table 3. At pH 3 to 5, the migration velocity of Cr was low and appeared to be unaffected by groundwater pH, reflecting the insolubility of Cr(OH)₃. For Cd, Cu, Ni and Zn, the migration velocity more than halved for each unit increase in groundwater pH. The decreasing migration velocities of Cd, Cu, Ni and Zn with increasing pH are likely to be a combination of stronger adsorption to iron hydroxide phases and increased precipitation as hydroxy-carbonate phases.

With respect to the transport of metals through estuarine sediments, the neutralisation of acidic groundwater by deeper sediments is expected to result in the removal (precipitation and adsorption) of the metals from the groundwater in the order Cr>Pb>>Cu>Cd/Ni/Zn (Mineql, 1998). Consequently, for a groundwater containing equal concentrations of these metals, the efflux of Cd, Ni and Zn (from sediments to overlying waters) would be expected to occur well before the efflux of Cr, Cu and Pb. Significant transport and groundwater-derived efflux of Cr, Cu and Pb from sediments would not be expected until the sediments became quite acidic and the majority of strong metal binding sites were saturated.
Metal migration velocities were similar for groundwaters with low and medium metal concentrations (0.4/2 mg/L Cd/Cr/Ni, 2/10 mg/L Cu/Pb/Zn), but increased by 60 to 180% as groundwater metal concentrations were increased from medium to high metal concentrations (2/10 mg/L Cd/Cr/Ni, 10/50 mg/L Cu/Pb/Zn) (data not shown). This indicated that, over the duration of the experiments, the metal-binding phases in the sediments (that attenuated metal transport) may have started to become saturated at the highest groundwater metal concentrations. This was supported by calculations that indicated that metal retention (as a percent of total metal throughput) decreased as groundwater metal concentrations increased. In general, for groundwaters of pH 3, metal migration velocities were ~0.5-2% (Cr, Pb), 1-6% (Cu) and 4-13% (Cd, Ni, Zn) of the total groundwater velocity.

Organically-complexed metals were not considered in the current study, but are known to enhance metal solubility and migration velocities (Christensen et al., 1996; Jensen and Christensen, 1999; Christensen et al., 2001).

3.5 Effect of reduced groundwater components and sediment sulfide phases on metal transport

Groundwater frequently contains high (100 mg/L range) dissolved iron and manganese concentrations (Christensen et al., 2001; Charette and Sholkovitz, 2002). The effect of groundwater Fe(II) (5-10 mg/L) and Mn(II) (1-5 mg/L) concentrations on metal migration velocities was investigated. Retention of groundwater Fe(II) occurred mostly in the bottom 5 cm of the 20 cm sediment columns, while Mn(II) retention occurred throughout the sediment columns, with peak retention in the middle of the columns (approximately 10 cm deep). This is consistent with the slower rate of oxidation of Mn(II) than Fe(II) (Millero, 2001). Although the redox potential (Eh) of the sediments was not measured, the oxidative precipitation of groundwater Fe(II) as iron hydroxide phases (e.g. FeOOH, Fe(OH)_3) was expected to have caused a corresponding increase in sediment Eh. Previous studies have shown that metal additions to anoxic or sub-oxic sediments cause both decreases in pH and increases in Eh as introduced metals displace Fe(II) and subsequent oxidation and hydrolysis reactions proceed (Simpson et al., 2004).

The precipitation of groundwater-derived iron and manganese in the sediments would be expected to increase the density of metal binding sites and reduce metal migration velocities. Alternatively, the formation of iron and manganese hydroxide colloids would be expected to facilitate the transport of adsorbed metals and increase metal migration velocities (Jensen and Christensen, 1999; Christensen et al. 2001). In the present study, increased concentrations of Fe(II) and Mn(II) in
the groundwater, and the oxidative precipitation of these elements as hydroxide phases in the sediment columns, was not observed to affect metal mobility through the sediments.

The passage of pH 5 groundwaters through the sediments resulted in the rapid dissolution of acid-volatile sulfide (AVS) phases. After 2 h, the sediments had lost approximately 60% of the 40 µmol/g of AVS originally present and a distinct profile in AVS was observed from the bottom (1.5 µmol/g) to the top (37 µmol/g) of the 20-cm deep sediment columns. After 6 h, the sediments contained <1 µmol/g in the lower 18 cm of the sediment columns and ~2 µmol/g in the top 2 cm, and after 24 h, <0.5 µmol/g AVS was present in any of the sediments. The rate of loss of AVS was >10 µmol/g/h when exposed to a pH 5 groundwater flow rate of 80 m/year. As the dissolution of AVS occurred, the oxidation of sulfide and Fe(II) would have caused large increases in sediment redox potential (not measured).

Metal transport in the acidic groundwater did not appear to be affected by the presence of AVS in the sediments (data not shown). For groundwaters that are less acidic, AVS is expected to significantly decrease metal transport (Simpson et al., 1998). Because AVS is an important phase controlling metal bioavailability in sediments (Di Toro et al., 1992; Simpson 1998), the loss of AVS due to the passage of acidified groundwater through sediments will have important implications for sediment quality.

3.6 Implications for sediment dwelling organisms

This study investigated factors that control the transport and retention of groundwater-derived metals as they efflux through estuarine surface sediments. Because surface sediments in estuaries represent an important habitat to many benthic organisms, the passage of contaminated groundwater through these environments may represent a major source of contaminant exposure for many organisms. Potential exposure pathways include ingestion of sediment or detritus material contaminated by groundwater or filtration of overlying waters that contain elevated concentrations of contaminants due to groundwater induced fluxes (Wang and Fisher, 1999).

Large spatial variations in the grain size of naturally-deposited estuarine sediments are common. This study showed that groundwater will preferentially select flow paths through the most coarsely-grained and permeable sediment substrate accessible. Consequently, fine-grained and silty sediments (i.e. low permeability) would be expected to remain relatively unaffected by contaminated groundwater flows due to physical resistance of groundwater passage through these substrates.

Prolonged exposure to flows of acidic, metal-contaminated groundwater through the more permeable
sediments would be expected to result in high metal concentrations at all depths. The acidification and loss of metal-binding phases (Fe and Mn (hydr)oxides and Fe sulfides) from these sediments will increase the bioavailability of sediment metals. The preferential flow of groundwater through the more permeable sediments may result in the physical removal and erosion of fine-grained sediment materials, thus leading to further increases in permeability, a greater rate of loss of metal-binding phases, greater migration of metals to the marine environment and a lessening of the sediment buffering capacity.

Benthos resident in sediments of high permeability (sandy sediments) will be expected to be most affected by emerging groundwater. Fine-grained and low permeability sediments would be expected to provide more hospitable conditions (lower groundwater metal concentrations and less acidic pH) for organisms. Organisms that create deep burrows may, however, increase their risk of exposure to contaminated groundwater if they burrow into coarse-grained sediments deposited below silty surface sediments. Organisms that are active filter feeders, or organisms that irrigate their burrows, will receive increased exposure to groundwater contaminants that exit the sediments to overlying water.

Acknowledgements

The authors thank Graeme Batley for constructive comments on this article. We thank David Bishop for assistance with experiments. The project was supported, in part, by a research grant received from the New South Wales Environmental Trust, Australia.
References


Table 1. Physical properties of the sand-sediment mixtures and sediment permeability in the 4-column systems.

<table>
<thead>
<tr>
<th>Sediment properties</th>
<th>Column 1</th>
<th>Column 2</th>
<th>Column 3</th>
<th>Column 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>GP sediment:sand</td>
<td>1:0</td>
<td>1:1</td>
<td>1:2</td>
<td>1:3</td>
</tr>
<tr>
<td>% &gt;600 µm</td>
<td>19</td>
<td>59</td>
<td>73</td>
<td>79</td>
</tr>
<tr>
<td>% &lt;180 µm</td>
<td>17</td>
<td>8</td>
<td>6</td>
<td>4.3</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>62</td>
<td>46</td>
<td>43</td>
<td>38</td>
</tr>
<tr>
<td>Total flow rate a</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>m/y</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Low</td>
<td>9</td>
<td>2.41</td>
<td>4.25</td>
<td>11.2</td>
</tr>
<tr>
<td>Medium</td>
<td>54</td>
<td>1.16</td>
<td>9.59</td>
<td>76.5</td>
</tr>
<tr>
<td>High</td>
<td>700</td>
<td>21.6</td>
<td>221</td>
<td>740</td>
</tr>
</tbody>
</table>

a Through the 4-column system.  
b Single sediment columns within the 4-column system.

Table 2. Metal migration velocities through sediments of differing permeability. The groundwater was pH 3 and the total flow rate through the 4-column system was 9 m/y.

<table>
<thead>
<tr>
<th>GP sediment:sand mixture</th>
<th>Flow rate a m/y</th>
<th>Metal migration velocity, m/y</th>
<th>Cd</th>
<th>Cr</th>
<th>Cu</th>
<th>Ni</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:0 (least permeable)</td>
<td>2.4</td>
<td>0.22</td>
<td>0.18</td>
<td>0.11</td>
<td>0.29</td>
<td>0.29</td>
<td></td>
</tr>
<tr>
<td>1:1</td>
<td>4.3</td>
<td>0.25</td>
<td>0.29</td>
<td>0.18</td>
<td>0.32</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>1:2</td>
<td>11</td>
<td>0.65</td>
<td>0.14</td>
<td>0.40</td>
<td>0.68</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>1:3 (most permeable)</td>
<td>18</td>
<td>1.5</td>
<td>0.22</td>
<td>0.90</td>
<td>1.3</td>
<td>1.4</td>
<td></td>
</tr>
</tbody>
</table>

Table 3. The effect of groundwater pH on metal migration velocities through a 2:1 mixture of GP sediment:sand. The groundwater flow rate was 80 m/y.

<table>
<thead>
<tr>
<th>Groundwater pH</th>
<th>Metal migration velocity, m/y</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cd</td>
</tr>
<tr>
<td>3</td>
<td>3.1</td>
</tr>
<tr>
<td>4</td>
<td>1.0</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
</tr>
</tbody>
</table>
Figure 1. Four-column system constructed from four small polycarbonate tubes (35 mm diameter, 600 mm length) positioned tightly within in a wider Perspex tube (92 mm diameter, 500 mm length). A: seawater, B: perforated Perspex retainer, C: sediment (20 cm), D: silicon sealant, E: sand (5 cm), F: groundwater inlet tube.
Figure 2. pH of sediments in the 4-column system (GP sediment:sand 1:0, 1:1, 1:2, and 1:3) following the passage of artificial groundwater of pH 3 (flow rate of 9 m/year for 773 h). The variation in pH measured in replicate experiments was <0.15 pH units.

Figure 3. Acid-neutralising capacity of 1:2 GP-sediment:sand mixtures following the passage of artificial groundwater of pH 3 at a flow rate of 80 m/y for 1 (○), 2 (●), 4 (■) and 7 days (△). The variation in ANC measured in replicate experiments was <0.1 µmol/g.
Figure 4. Breakthrough of metals (as a percent of total groundwater metals entering the sediments) during the passage of artificial groundwater of pH 3 at a flow rate of 9 m/y through a 1:3 GP-sediment:sand mixture. The variation in % breakthrough measured in replicate experiments was <5%.
Figure 5. Attenuation of Zn, Cu and Pb by a 1:2 GP-sediment:sand mixture after 1 day (▲), 2 days (×), 4 days (○) and 7 days (■). The groundwater contained metal mixtures of Cd/Cr/Cu/Ni/Pb/Zn at 2/2/10/2/10/10 mg/L (pH 3), respectively, and the flow rate was 80 m/year. Error bars represent the standard deviation of replicate experiments.
Figure 6. Effect of metal concentration on the attenuation of Ni, Cu and Cr by a 1:2 GP-sediment:sand mixture. The groundwaters (pH 3) contained ‘high’ (●) 50/10/50 mg/L, ‘medium’ (△) 10/2/10 mg/L and ‘low’ (■) 2/0.4/2 mg/L concentrations of Cu/Ni/Zn, respectively. The groundwater flow rate was 80 m/year for 168 h. Error bars represent the standard deviation of replicate experiments.
Figure 7. The effect of groundwater flow rate on the attenuation of Cd, Cu and Cr by sediment columns containing a 1:3 GP-sediment:sand mixture. The flow rates were 9 (×), 54 (○) and 700 m/year (∆) and the groundwater was pH 3 with Cd/Cr/Cu concentrations of 10/10/50 mg/L, respectively. The duration of the experiments was such that approximately 1.5 L of artificial metal-contaminated groundwater passed through each column.
Figure 8. Attenuation of Cd, Cu and Cr by sediments of differing permeability: GP-sediment:sand mixtures 1:0 (X, least permeable), 1:1 (▲), 1:2 (○) and 1:3 (●, most permeable) (Table 1). The groundwater was pH 3 and Cd/Cr/Cu concentrations were 10/10/50 mg/L, respectively. The flow rate was 9 m/year for a 96-h duration.