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

Abstract

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.

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1 **Processes controlling metal transport and retention as metal-contaminated groundwaters efflux**
2 **through estuarine sediments.**

3

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

39

40 **Key Words—** Groundwater, Metals, Transport, Retention, Sediment

41

42 **1 Introduction**

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

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

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

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

73

74 2 Materials and methods

75 All glass and plasticware was cleaned by soaking in 10% (v/v) HNO₃ (Trace Pur, Merck) for
76 >24 h followed by rinsing with deionised water (Milli-Q, Millipore). All laboratory-ware used for
77 dissolved metals sampling and analysis was cleaned in a Class-100 laminar-flow cabinet (metal-free
78 HWS, Clyde-Apac). All chemicals were analytical reagent grade or equivalent analytical purity.
79 Deoxygenated solutions were prepared by bubbling solutions with oxygen-free nitrogen gas for >8 h
80 to give dissolved oxygen concentrations <0.1 mg/L. These solutions were stored in a nitrogen gas-
81 filled glove box.

82 Measurements of pH (calibrated against pH 4 and 7 buffers) were made as described previously
83 (Simpson and Batley, 2003). All water filtrations were made using a plastic syringe and plastic
84 encapsulated 0.45 µm cellulose nitrate membrane filters (25 mm, Minisart, Sartorius) that were acid-
85 washed with 20 mL of 2% HNO₃ (Trace Pur, Merck) and rinsed with 40 mL of deionised water before
86 use. Dissolved metal concentrations were determined by inductively coupled plasma atomic emission
87 spectrometry (ICP-AES) (Spectroflame EOP, Spectro Analytical Instruments) calibrated with matrix-
88 matched standards according to Simpson et al. (2002). High-purity Milli-Q deionised water (18
89 MΩ/cm) was used to dilute analysis solutions.

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

95 Sediment porosity, wet density, and moisture content were determined according to standard
96 methods (Mudroch et al., 1997). Sediment size fractionation determinations have been described
97 previously (Simpson et al., 1998). Acid-volatile sulfide (AVS) was determined according to Simpson
98 (2001). Acid-extractable metals were determined by addition of 20.0 mL of 1 M HCl to 0.400 g of
99 wet sediment, briefly shaking and analysis of filterable metals (by ICP-AES) after 24 h extraction.
100 The sediment pH and acid-neutralising capacity (ANC) were measured on a mixture of 2.00 g wet
101 sediment and 2.00 g deoxygenated Milli-Q water. pH measurements were made five minutes after
102 mixing in a nitrogen filled glove box. ANC measurements were made by measuring the pH 24 h after
103 the addition of 2.00 mL of 0.001 M HCl (pH 3) to the Milli-Q wetted sediment. The ANC was
104 calculated as, $ANC = 0.001 - 10^{(-pH)}$ (in µmol/g dry weight). Duplicate analyses and measurements
105 were performed on 10% of all samples.

106

107 *2.1 Artificial groundwater compositions*

108 Artificial groundwater solutions were prepared by dilution of 1000 mg/L metal stock solutions
109 with deoxygenated Milli-Q water containing 25 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ and 50 mg/L of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.
110 Chloride salts were used for Cd, Cr, Cu, Fe and Mn, sulfate salts for Ni and Zn and a nitrate salt for
111 Pb. Groundwater solutions were acidified to pH 3, 4 or 5 using concentrated HCl and stored in a
112 nitrogen gas-filled glove box.

113

114 *2.2 Column experiments*

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

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

133 Single-column experiments used the smaller tubes and same sediment packing procedures as the
134 4-column system. A rubber bung, fixed in place with silicon sealant, was used to seal the base of the
135 single columns. Groundwater entered the base of the columns through a tube in the centre of the bung.

136 An airpump and fine tubing was used to bubble air into 20 cm of overlying water above the
137 sediment columns to maintain circulation. The groundwater inlet tubes were connected to peristaltic
138 pumps (Minipuls 3, Gilson) using 0.89 mm I.D. PCV pump tubing (A.I. Scientific, Australia).

139

140 2.3 *Sediment permeability and groundwater flow rate experiments*

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

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

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

159

160 2.4 *Groundwater flow duration, metal concentration and pH experiments*

161 Single-column systems were used to investigate the effects of flow time, metal concentration
162 and pH on sediment acidification and metal transport processes. The sediment mixtures comprised 1:2
163 GP-sediment:sand and the groundwater flow rate was 80 m/year (9.0 mL/h). To investigate the effect
164 of flow time, experiments were run for 24, 48, 96 and 168 h with groundwater of pH 3 and mixtures of
165 Cd/Cr/Cu/Ni/Pb/Zn at 10/10/50/10/50/50 mg/L, respectively. The 96-h treatment was run in
166 duplicate. To investigate the effect of pH, experiments were run for 168 h using groundwater of pH 3,
167 4 and 5 and metal mixtures of 5 mg/L Cd/Cr/Cu/Ni/Zn. The pH 4 experiment was run in duplicate.

168 To investigate the effect of metal concentration, experiments were run for 168 h using groundwater of
169 pH 3 and metal mixtures of Cd/Cr/Cu/Ni/Pb/Zn at ‘high’ (10/10/50/10/50/50 mg/L, respectively),
170 ‘medium’ (2/2/10/2/10/10 mg/L, respectively) and ‘low’ (0.4/0.4/2/0.4/2/2 mg/L, respectively)
171 concentrations. The medium metal concentration experiment was run in duplicate. At the end of each
172 experiment the cores were frozen, sectioned and analysed as described for the effect of sediment
173 permeability and flow rate experiments.

174

175 *2.5 Groundwater Fe(II) and Mn(II) experiments*

176 Single-column systems were used to investigate the effect of groundwater Fe(II) and Mn(II) on metal
177 transport. The sediment mixtures comprised 1:2 GP-sediment:sand and the groundwater flow rate was
178 80 m/year (9.0 mL/h). Experiments were run for 168 h using groundwater of pH 3 containing
179 2/2/10/2/10/10 mg/L Cd/Cr/Cu/Ni/Pb/Zn, respectively, and Fe(II)/Mn(II) at three different
180 concentrations: (i) 0/0, (ii) 5/1, or (iii) 20/5 mg/L, respectively. At the end of the experiments the
181 cores were treated and analysed as described for the effect of sediment permeability and flow rate
182 experiments.

183

184 *2.6 Effect of acidic groundwater on sediment sulfide phases*

185 Single-column systems were used to investigate the effect of acidic groundwater on the acid-volatile
186 sulfide (AVS) phases which are important for metal binding in sediments. A 1:2 GP-sediment:sand
187 mixture was spiked with sufficient dissolved sulfide (Na_2S) to result in an AVS concentration of
188 approximately 40 $\mu\text{mol/g}$ and equilibrated for three weeks before use. Deoxygenated groundwater of
189 pH 5 was pumped through the sulfide-spiked sediment columns at a rate of 9.0 mL/h for 2, 6 or 24
190 hours. AVS was analysed on sediment core sections at the completion of the experiments and
191 compared with the AVS concentration measured before groundwater exposure.

192

193 **3 Results and discussion**

194 *3.1 Sediment properties*

195 The Gray’s Point (GP) sediment comprised 46% water, 4.5% organic carbon (dry weight) and
196 had a particle size distribution: 11% <63 μm ; 6% 63-180 μm ; 64% 180-600 μm and 19% 600-1000
197 μm . The sediment pH was 7.3. The acid-extractable metal concentrations (in $\mu\text{g/g}$) were 1340 (Fe),
198 4.7 (Mn), 28 (Zn), 19 (Pb), 10 (Cu), 1.0 (Ni) and 0.3 (Cd) (Simpson et al., 2004). The sand that was
199 mixed with the GP sediment comprised 100% 600-1000 μm sized particles and <0.1% organic carbon.

200

201 *3.2 Effect of sediment permeability on groundwater flow rate and sediment acidification processes*

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

210 The magnitude of natural groundwater flow rates can be quite varied, both between sites and
211 between different flow paths within the same site. Tides, waves, storms, bioturbation and
212 anthropogenic activities will all affect groundwater discharge rates in coastal environments. In near-
213 shore aquifers, the upwards deflection of groundwater flows by salinity density gradients is expected
214 to result in a greater flow rate in the upper portion of shoreline sediments than the mean groundwater
215 flow rates throughout the aquifer (Lui et al., 2001). Submarine groundwater discharge rates have been
216 reported as ranging from 0.01 to 2630 m/year (Lui et al., 2001). The current study indicated that high
217 (500 m/year range) groundwater flow rates are only likely to occur in very sandy sediments and that
218 most of the groundwater will flow around (not through) fine-grained (silty) sediments until coarse-
219 grained (sandy) sediments are accessible for discharge to the overlying water environment.
220 Consequently, silty sediments should receive a lower exposure to groundwater contaminants.

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

231

232 3.3 *Effect of sediment and groundwater properties on metal transport through sediments*

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

247 The attenuation of groundwater metals by the sediments was characterised by measurements
 248 of the acid-extractable metals retained in the sediments at the completion of the experiments (Figures
 249 5-8). The attenuation of metal transport through the sediment columns reflected the properties of the
 250 sediments, the groundwater flow rate, sediment acidification and the adsorption and solubility
 251 characteristics of the metals. The depth profiles for Cd, Ni and Zn retention in the sediment columns
 252 were very similar in shape. The profiles for Cr and Pb retention were very similar in shape.

253 The attenuation of metals in the groundwater (by the sediments) increased in the order
 254 Cd<Ni~Zn<<Cu<<Cr~Pb. Reactive sulfide (AVS) concentrations were low in the sediments and the
 255 mobility of metals in the sediments was expected to be controlled by the solubility of carbonate
 256 (solubility of $\text{MeCO}_{3(s)}$: Ni>Zn>Cu>Cd>>Pb) and hydroxide (solubility of $\text{Me(OH)}_{2(s)}$:
 257 Cd>Ni>Zn>>Cu>>Pb>>Cr(OH)_{3(s)}) phases and adsorption onto iron hydroxide phases
 258 (Ni<Cd<Zn<<Cu<<Pb<<Cr (strongest adsorption)) (Mineql, 1998).

259 The increased duration of exposure of the sediments to the acidic groundwater decreased the
 260 attenuation of Cr, Cu, Ni and Zn, but had little effect on the attenuation of Cr and Pb over the duration
 261 of the experiments (Figure 5). This pattern was consistent with the observed metal-breakthrough into
 262 the overlying waters (Figure 4). The high retention of Cr and Pb reflected the high particle reactivity
 263 of these metals and the decreased solubility of these metals as the groundwater pH increased during

264 the passage through the sediments (Figure 2). The decreased attenuation (increased migration) of Cd,
265 Cu, Ni and Zn reflected the acidification of the deeper sediments and possibly the saturation of strong
266 metal binding sites in the deeper sediments. Past studies have found that the pH at which ~50% of a
267 metal is adsorbed to solid phases (the adsorption edge) occurs at pH 4.0 and 4.4 for Cr and Pb,
268 respectively, near pH 5.2 for Cu, and at 6.0, 6.3 and 6.8 for Cd, Zn and Ni, respectively (Stumm and
269 Morgan, 1996). This is consistent with the greater mobility of Cd, Ni and Zn as the acidity of the
270 deeper sediments increased. During the 7-day period of groundwater flow, the Fe and Mn
271 concentrations in the sediments decreased at a rate of 10 ± 1 and 0.05 ± 0.01 $\mu\text{g/g}$ sediment /day,
272 respectively. This indicated that iron and manganese phases (e.g. hydroxides) were being dissolved by
273 the acidic groundwater and was consistent with the loss of ANC over this time period (Figure 4).

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

285 The attenuation of the groundwater metals decreased with increasing groundwater flow rate
286 (Figure 7). Very little Cd, Ni and Zn was retained in the 1:3 GP-sediment:sand mixture at the highest
287 groundwater flow rate (1790 m/year, Table 1). At slower groundwater flow rates (18, 129 m/year),
288 Cd, Ni and Zn were retained in the upper sediments, but not in the deeper sediments which had
289 become acidified (Figure 7). At all flow rates, the movement of Cu was attenuated by the sediments,
290 however a greater amount of Cu was retained by the sediments at the slower flow rates. The transport
291 of Cr and Pb in the groundwaters was attenuated strongly by all sediment mixtures and at all flow
292 rates. Chromium and Pb were only observed to move through the most permeable sediment mixture
293 (1:3 GP-sediment:sand) at the highest flow rate.

294 Metal attenuation decreased as the permeability of the sediments increased (Figure 8) and
295 reflected the decreased abundance of metal adsorption sites (greater proportion of sand) and the
296 greater acidification of the more permeable sediments (Figure 2).

297

298 3.4 Metal migration velocities

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

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

311 Groundwater pH is expected to have a large effect on metal migration velocities (Christensen et
312 al., 2001). The effect of groundwater pH on the migration velocity of Cd, Cr, Cu, Ni and Zn is shown
313 in Table 3. At pH 3 to 5, the migration velocity of Cr was low and appeared to be unaffected by
314 groundwater pH, reflecting the insolubility of $\text{Cr}(\text{OH})_3$. For Cd, Cu, Ni and Zn, the migration velocity
315 more than halved for each unit increase in groundwater pH. The decreasing migration velocities of
316 Cd, Cu, Ni and Zn with increasing pH are likely to be a combination of stronger adsorption to iron
317 hydroxide phases and increased precipitation as hydroxy-carbonate phases.

318 With respect to the transport of metals through estuarine sediments, the neutralisation of acidic
319 groundwater by deeper sediments is expected to result in the removal (precipitation and adsorption) of
320 the metals from the groundwater in the order $\text{Cr} > \text{Pb} > \text{Cu} > \text{Cd}/\text{Ni}/\text{Zn}$ (Mineql, 1998). Consequently,
321 for a groundwater containing equal concentrations of these metals, the efflux of Cd, Ni and Zn (from
322 sediments to overlying waters) would be expected to occur well before the efflux of Cr, Cu and Pb.
323 Significant transport and groundwater-derived efflux of Cr, Cu and Pb from sediments would not be
324 expected until the sediments became quite acidic and the majority of strong metal binding sites were
325 saturated.

326 Metal migration velocities were similar for groundwaters with low and medium metal
327 concentrations (0.4/2 mg/L Cd/Cr/Ni, 2/10 mg/L Cu/Pb/Zn), but increased by 60 to 180% as
328 groundwater metal concentrations were increased from medium to high metal concentrations (2/10
329 mg/L Cd/Cr/Ni, 10/50 mg/L Cu/Pb/Zn) (data not shown). This indicated that, over the duration of the
330 experiments, the metal-binding phases in the sediments (that attenuated metal transport) may have
331 started to become saturated at the highest groundwater metal concentrations. This was supported by
332 calculations that indicated that metal retention (as a percent of total metal throughput) decreased as
333 groundwater metal concentrations increased. In general, for groundwaters of pH 3, metal migration
334 velocities were ~0.5-2% (Cr, Pb), 1-6% (Cu) and 4-13% (Cd, Ni, Zn) of the total groundwater
335 velocity.

336 Organically-complexed metals were not considered in the current study, but are known to
337 enhance metal solubility and migration velocities (Christensen et al., 1996; Jensen and Christensen,
338 1999; Christensen et al., 2001).

339
340 *3.5 Effect of reduced groundwater components and sediment sulfide phases on metal transport*
341 Groundwater frequently contains high (100 mg/L range) dissolved iron and manganese concentrations
342 (Christensen et al., 2001; Charette and Sholkovitz, 2002). The effect of groundwater Fe(II) (5-10
343 mg/L) and Mn(II) (1-5 mg/L) concentrations on metal migration velocities was investigated.
344 Retention of groundwater Fe(II) occurred mostly in the bottom 5 cm of the 20 cm sediment columns,
345 while Mn(II) retention occurred throughout the sediment columns, with peak retention in the middle of
346 the columns (approximately 10 cm deep). This is consistent with the slower rate of oxidation of
347 Mn(II) than Fe(II) (Millero, 2001). Although the redox potential (Eh) of the sediments was not
348 measured, the oxidative precipitation of groundwater Fe(II) as iron hydroxide phases (e.g. FeOOH,
349 Fe(OH)₃) was expected to have caused a corresponding increase in sediment Eh. Previous studies
350 have shown that metal additions to anoxic or sub-oxic sediments cause both decreases in pH and
351 increases in Eh as introduced metals displace Fe(II) and subsequent oxidation and hydrolysis reactions
352 proceed (Simpson et al., 2004).

353 The precipitation of groundwater-derived iron and manganese in the sediments would be
354 expected to increase the density of metal binding sites and reduce metal migration velocities.
355 Alternatively, the formation of iron and manganese hydroxide colloids would be expected to facilitate
356 the transport of adsorbed metals and increase metal migration velocities (Jensen and Christensen,
357 1999; Christensen et al. 2001). In the present study, increased concentrations of Fe(II) and Mn(II) in

358 the groundwater, and the oxidative precipitation of these elements as hydroxide phases in the sediment
359 columns, was not observed to affect metal mobility through the sediments.

360 The passage of pH 5 groundwaters through the sediments resulted in the rapid dissolution of
361 acid-volatile sulfide (AVS) phases. After 2 h, the sediments had lost approximately 60% of the 40
362 $\mu\text{mol/g}$ of AVS originally present and a distinct profile in AVS was observed from the bottom (1.5
363 $\mu\text{mol/g}$) to the top (37 $\mu\text{mol/g}$) of the 20-cm deep sediment columns. After 6 h, the sediments
364 contained $<1 \mu\text{mol/g}$ in the lower 18 cm of the sediment columns and $\sim 2 \mu\text{mol/g}$ in the top 2 cm, and
365 after 24 h, $<0.5 \mu\text{mol/g}$ AVS was present in any of the sediments. The rate of loss of AVS was >10
366 $\mu\text{mol/g/h}$ when exposed to a pH 5 groundwater flow rate of 80 m/year. As the dissolution of AVS
367 occurred, the oxidation of sulfide and Fe(II) would have caused large increases in sediment redox
368 potential (not measured).

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

375

376 *3.6 Implications for sediment dwelling organisms*

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

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

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

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

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411

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

Sediment properties	Column 1	Column 2	Column 3	Column 4	
GP sediment:sand	1:0	1:1	1:2	1:3	
% >600 μm	19	59	73	79	
% <180 μm	17	8	6	4.3	
Porosity (%)	62	46	43	38	
Total flow rate ^a	Flow rates (relative permeability), m/y ^b				
m/y	Column 1	Column 2	Column 3	Column 4	
Low	9	2.41	4.25	11.2	18.4
Medium	54	1.16	9.59	76.5	129
High	700	21.6	221	740	1790

457 ^a Through the 4-column system. ^b Single sediment columns within the 4-column system.458
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461**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.**

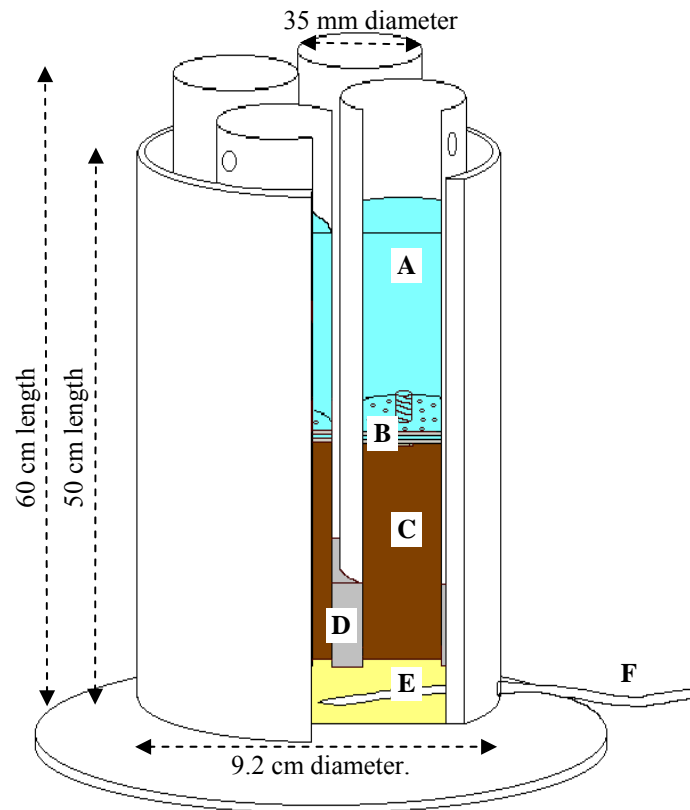
GP sediment:sand mixture	Flow rate ^a m/y	Metal migration velocity, m/y				
		Cd	Cr	Cu	Ni	Zn
1:0 (least permeable)	2.4	0.22	0.18	0.11	0.29	0.29
1:1	4.3	0.25	0.29	0.18	0.32	0.32
1:2	11	0.65	0.14	0.40	0.68	0.68
1:3 (most permeable)	18	1.5	0.22	0.90	1.3	1.4

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467**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.**

Groundwater pH	Metal migration velocity, m/y				
	Cd	Cr	Cu	Ni	Zn
3	3.1	0.6	1.1	3.2	3.4
4	1.0	0.4	0.5	1.5	1.4
5	0.5	0.5	0.1	0.8	0.7

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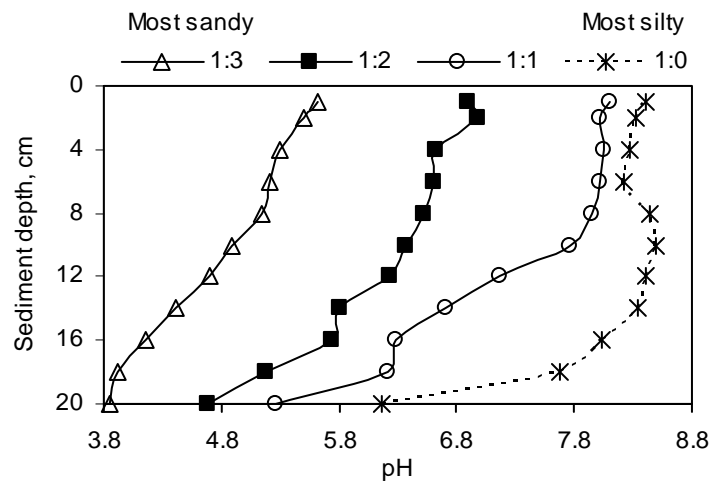
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476 Figure 1. Four-column system constructed from four small polycarbonate tubes (35 mm diameter, 600
 477 mm length) positioned tightly within in a wider Perspex tube (92 mm diameter, 500 mm length). A:
 478 seawater, B: perforated Perspex retainer, C: sediment (20 cm), D: silicon sealant, E: sand (5 cm), F:
 479 groundwater inlet tube.

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484 Figure 2. pH of sediments in the 4-column system (GP sediment:sand 1:0, 1:1, 1:2, and 1:3) following

485 the passage of artificial groundwater of pH 3 (flow rate of 9 m/year for 773 h). The variation in pH

486 measured in replicate experiments was <0.15 pH units.

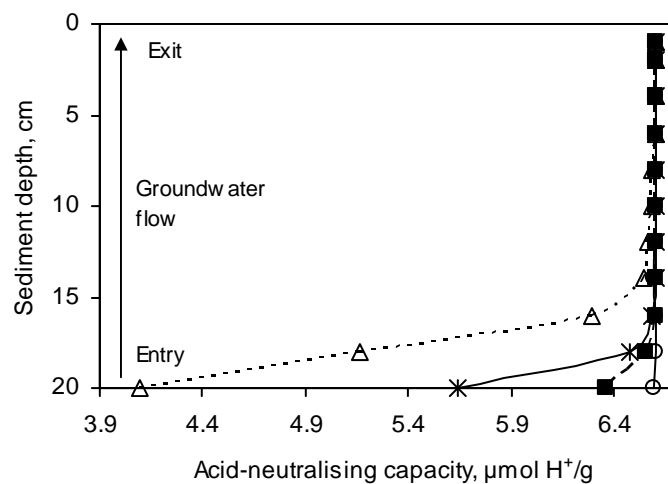
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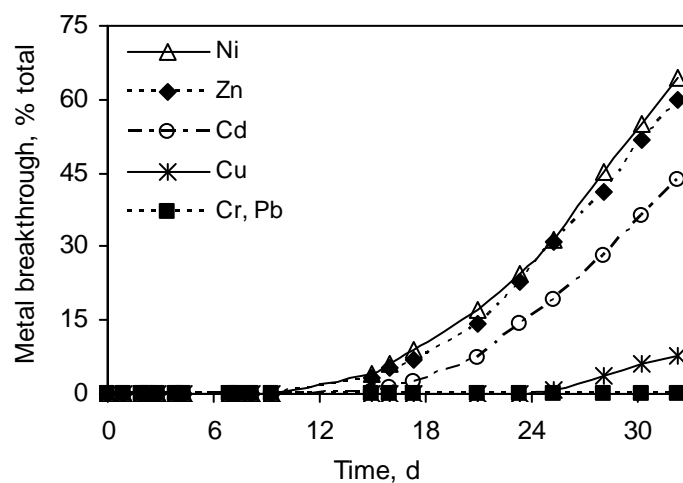
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495 Figure 3. Acid-neutralising capacity of 1:2 GP-sediment:sand mixtures following the passage of

496 artificial groundwater of pH 3 at a flow rate of 80 m/y for 1 (O), 2 (*), 4 (■) and 7 days (Δ). The

497 variation in ANC measured in replicate experiments was <0.1 μmol/g.

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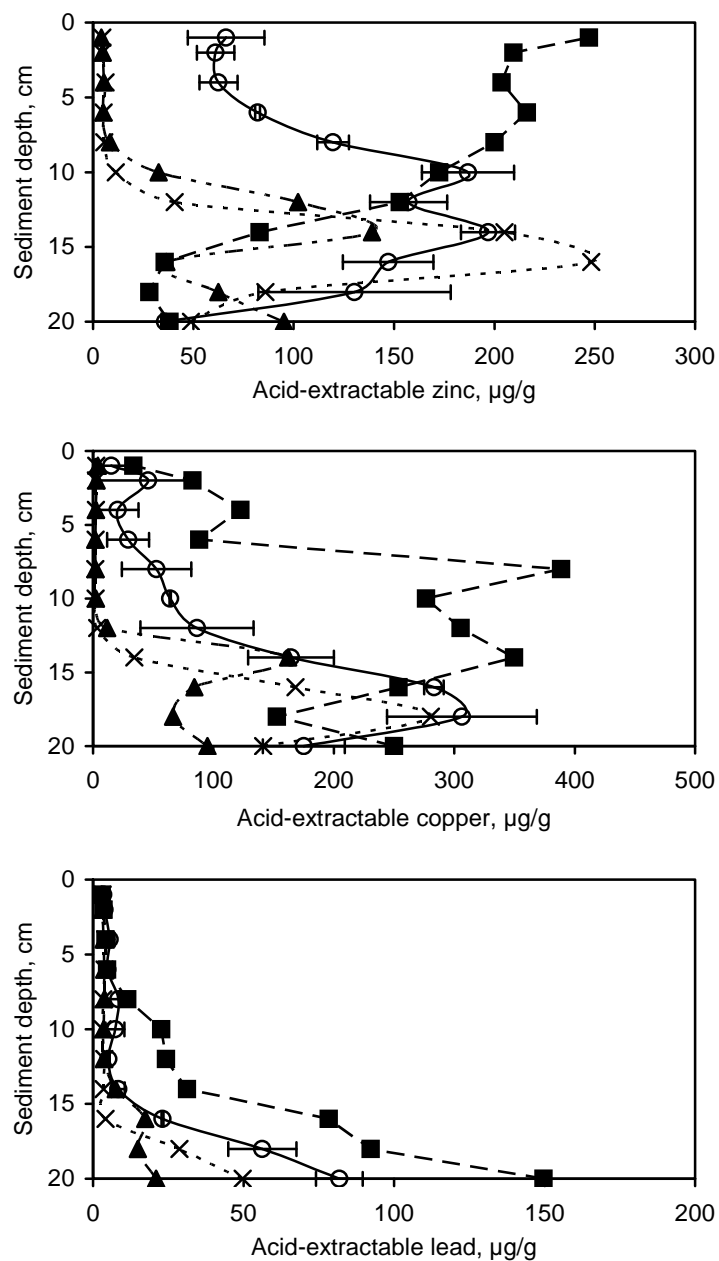
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503 Figure 4. Breakthrough of metals (as a percent of total groundwater metals entering the sediments)
504 during the passage of artificial groundwater of pH 3 at a flow rate of 9 m/y through a 1:3 GP-
505 sediment:sand mixture. The variation in % breakthrough measured in replicate experiments was <5
506 %.

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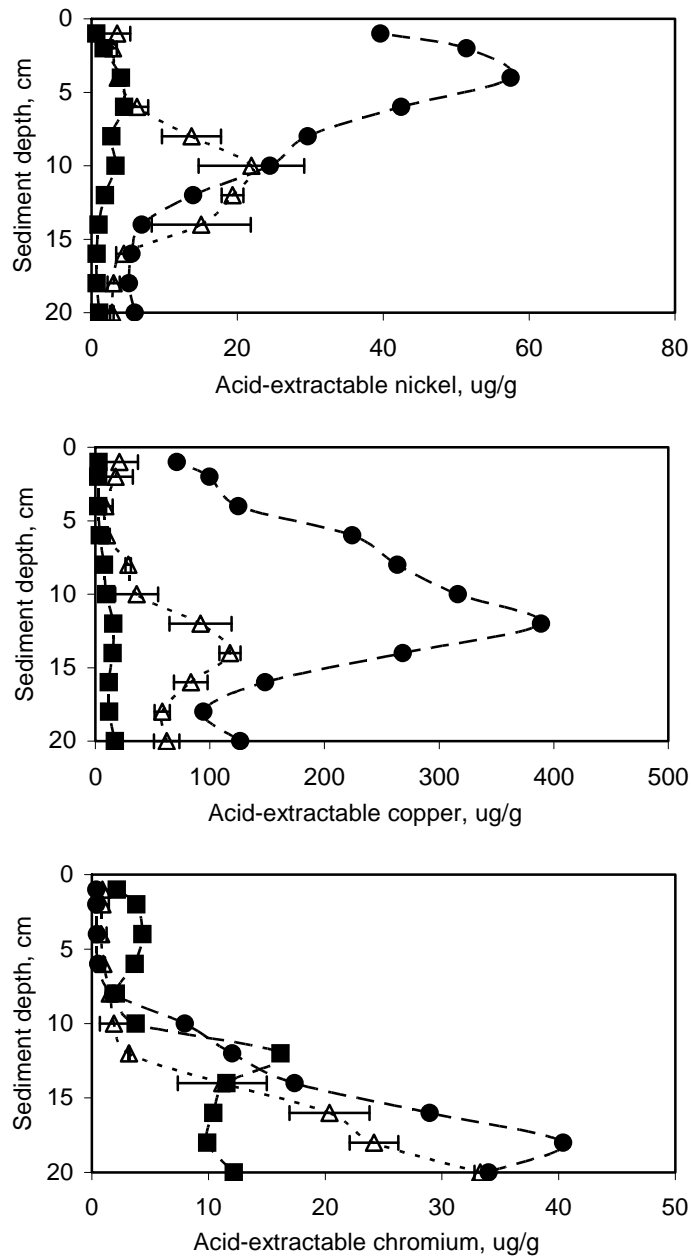
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 512 Figure 5. Attenuation of Zn, Cu and Pb by a 1:2 GP-sediment:sand mixture after 1 day (▲), 2 days
 513 (×), 4 days (○) and 7 days (■). The groundwater contained metal mixtures of Cd/Cr/Cu/Ni/Pb/Zn at
 514 2/2/10/2/10/10 mg/L (pH 3), respectively, and the flow rate was 80 m/year. Error bars represent the
 515 standard deviation of replicate experiments.

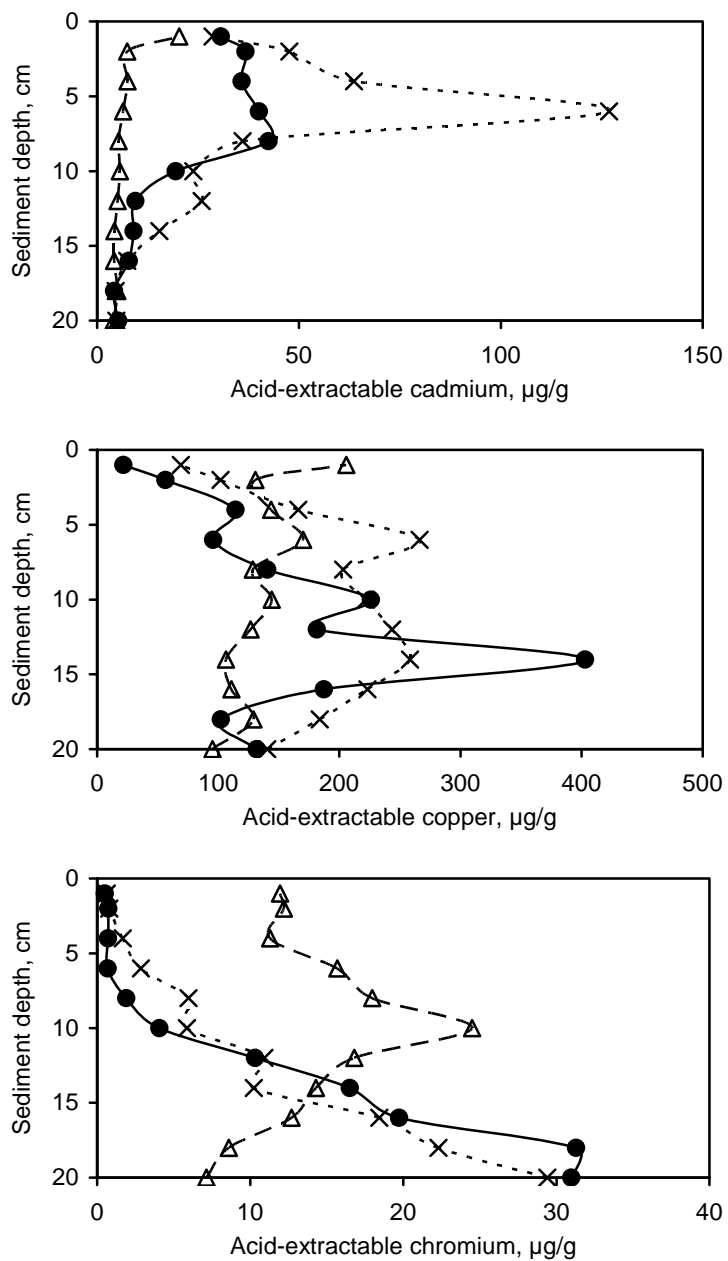
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Figure 6. Effect of metal concentration on the attenuation of Ni, Cu and Cr by a 1:2 GP-sediment:sand mixture. The groundwaters (pH 3) contained 'high' (●) 50/10/50 mg/L, 'medium' (△) 10/2/10 mg/L and 'low' (■) 2/0.4/2 mg/L concentrations of Cu/Ni/Zn, respectively. The groundwater flow rate was 80 m/year for 168 h. Error bars represent the standard deviation of replicate experiments.

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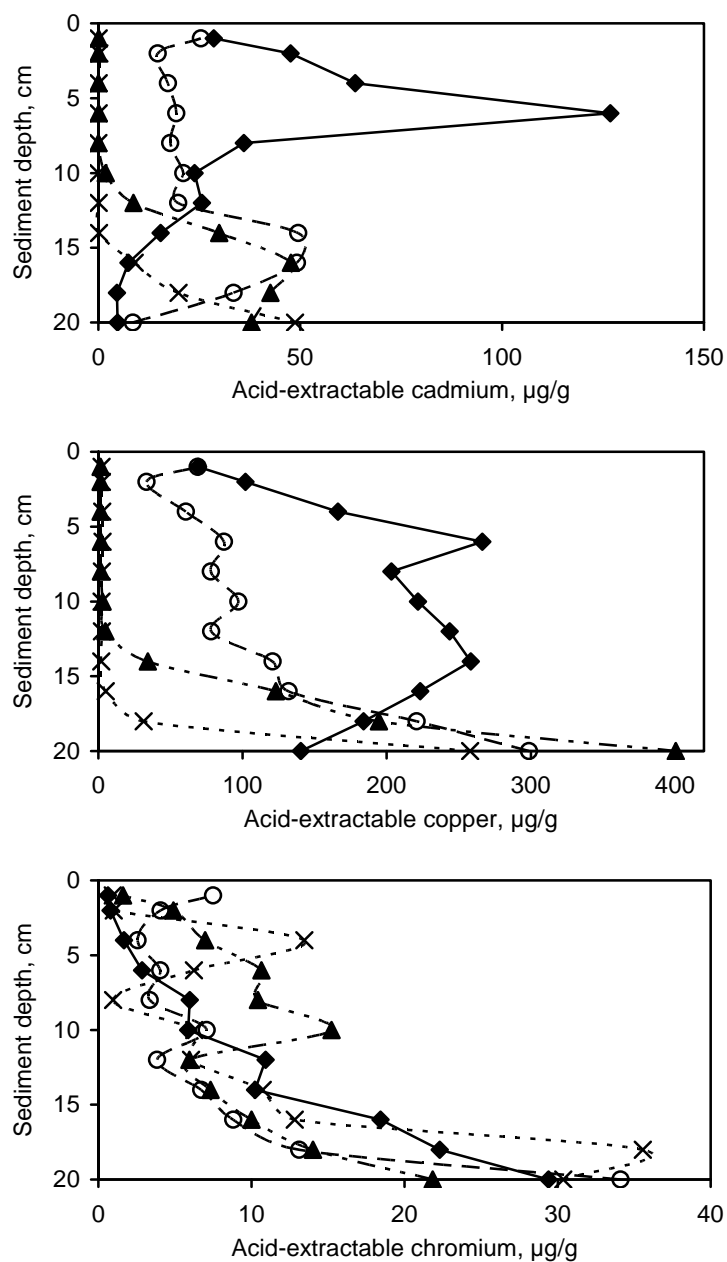
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532 Figure 7. The effect of groundwater flow rate on the attenuation of Cd, Cu and Cr by sediment
 533 columns containing a 1:3 GP-sediment:sand mixture. The flow rates were 9 (×), 54 (●) and 700
 534 m/year (△) and the groundwater was pH 3 with Cd/Cr/Cu concentrations of 10/10/50 mg/L,
 535 respectively. The duration of the experiments was such that approximately 1.5 L of artificial metal-
 536 contaminated groundwater passed through each column.

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542 Figure 8. Attenuation of Cd, Cu and Cr by sediments of differing permeability: GP-sediment:sand
 543 mixtures 1:0 (×, least permeable), 1:1 (▲), 1:2 (○) and 1:3 (◆, most permeable) (Table 1). The
 544 groundwater was pH 3 and Cd/Cr/Cu concentrations were 10/10/50 mg/L, respectively. The flow rate
 545 was 9 m/year for a 96-h duration.