

Attenuation and transport characteristics of cadmium, zinc and lead in selected New Zealand aquifer systems

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Abstract

This article summarises major findings from the authors' research into the attenuation and transport of three cationic heavy metals—Cd, Zn and Pb—in alluvial gravel, pumice sand and coastal sand, the major types of aquifer in New Zealand. Results obtained from field, laboratory column and batch adsorption experiments, as well as model simulations, are presented and compared. The processes that govern the attenuation and transport of these metals in aquifer systems and the factors that influence these processes are discussed.

Our studies show that the overall adsorption capacities of pumice sand and coastal sand were similar but that the adsorption capacity of alluvial gravel was lower. In addition, the transport characteristics of Cd and Zn were alike, with similar retardation factors, but Pb was one to two orders of magnitude more retarded. Metal adsorption in our experiments was a nonlinear, kinetic process, with desorption rates that were two to three orders of magnitude slower than their relative adsorption rates. The retardation factor was inversely related to flow velocity and metal concentration, but positively related to the pH level of the groundwater. The values of the adsorption parameters of the heavy metals followed the order of batch > column > field. Therefore, care should be taken when laboratory results are used to predict the movement of heavy metals in the

field. In addition, when bacteria were present at high concentrations, the mean transport velocity of Cd was enhanced up to 28 times. As contaminants generally co-exist with colloids in contaminated groundwater, the transport of heavy metals could be dramatically accelerated if the metal is adsorbed to mobile bacteria and other colloids. The kinetic desorption and colloid-facilitated transport of heavy metals are worthy of future research, as they have important implications in risk assessments of groundwater quality and the design and operation of site remediation programmes.

Introduction

Groundwater contamination by heavy metals occurs in many countries, including New Zealand. In some areas of New Zealand, groundwater is locally contaminated by heavy metals from industrial sites, mining, timber factories, landfills and agrochemicals. One of the worst examples of groundwater contamination in New Zealand is at the abandoned Tui Mine in Te Aroha, where the groundwater is contaminated by Cu, Pb, Zn, Cd, Fe, Mn, As and Hg. Here the streams that are recharged from the polluted groundwater from tailing leachates and mineshaft drainage have become lifeless (Pang, 1995). At some timber treatment sites, groundwater contamination by Cu, Cr and As has been reported (Armishaw *et al.*, 1994). Heavy metal concentrations are also naturally

elevated in some groundwaters from volcanic geological formations.

Hunter (1992) provided an overview of trace elements in aquatic systems in New Zealand, and Smith (1985) reviewed the sources of heavy metal input to the New Zealand aquatic environment. These sources include geothermal activity and geological weathering, and human transport (e.g., Pb and vehicle corrosion products), industry, timber treatment (As, Cu and Cr), metal working and finishing (Ni and Zn), mining, industrial and municipal wastes, agricultural activities (including animal dietary additives, pesticide residues and fertiliser runoff), tanneries (containing Cr and Zn), carpet mills (organic metallic dyes used containing Cu, Cr, and Ni), textile dyeing and wool-scouring (Cr, Cu, Pb and Zn), and dairy factory wastes (Cu, Cr, Ni and Zn).

Information on the attenuation and transport of heavy metals in aquifer systems is essential for the management of groundwater resources and for the design of monitoring programmes and remediation regimes. A few studies in this topic have been undertaken in New Zealand. For example, Pang (1995) studied the relative attenuation of heavy metals (Cu, Pb, Zn, Cd, Fe, Mn) in the andesite volcanic aquifer in the Te Aroha area, using laboratory batch studies. She found that Cd was the most mobile metal of all the metals examined. Hinton and Close (1998) studied Pb adsorption onto the coating (composed mainly of iron) of alluvial gravels, using batch experiments and X-ray photoelectron spectroscopy. They found that lead is more rapidly adsorbed by coated gravels than by non-coated gravels, and that the adsorption of lead is non-linear. As a part of the National Groundwater Monitoring Programme, a preliminary survey of heavy metals in groundwater was carried out in 1998 (Rosen, 2001). Eighty-seven samples from 13 regions were analysed for As, Cr, Cu and Pb; As was detected in 23% of the samples at

concentrations 1–12 µg/l. Anomalously high concentrations of As (54 µg/l) were found in Canterbury during the survey. A follow-up investigation revealed that other wells in the area were also contaminated with As, and the source was found to be an old sheep foot trough site (Rosen, 2001). Arsenic-based chemicals were used extensively in sheep and cattle dips for the control of parasites in the first half of the 20th century and many thousands of these sites still exist throughout the country. The detection of Cr and Pb in the samples was 17% and 93%, respectively, with concentrations mostly below 1 µg/l and the highest concentration at 6 µg/l. Cu was detected in all regions at an average concentration of 3 µg/l; the highest concentration was 31 µg/l (Rosen, 2001).

In the past few years, we have investigated the attenuation and transport characteristics (adsorption, desorption, precipitation and migration) of a few cationic heavy metals (Cd, Zn and Pb) in alluvial gravel, pumice sand and coastal sand aquifer media, using laboratory batch/column experiments and field-tracer studies. These studies have included (1) bacteria-facilitated Cd transport in alluvial gravel aquifer media on a field scale (Pang and Close, 1999a) and a laboratory scale (Pang *et al.*, 2004a), (2) the effects of the scale of transport (Pang and Close, 1999b) on Cd transport, (3) the effects of flow velocity on Cd, Zn and Pb transport (Pang *et al.*, 2002), and (4) Cd transport in pumice sand aquifer media (Pang *et al.*, 2004b). Additional batch isotherm adsorption studies have also been undertaken. Cd was used in most of our studies, as it is a toxic, nonessential (to human health), trace groundwater constituent and is among the most mobile heavy metals in groundwater.

The purpose of this paper is to summarise the major research findings from our previous studies and to present the results obtained from additional batch studies. These research findings should provide useful information

for the management of similar aquifer systems for use in resource management, land-use planning, the design of monitoring programs, risk analysis and site remediation.

Materials and methods

Selected aquifer media

Alluvial gravel

Alluvial gravel aquifers are a major type of aquifer in New Zealand and they are widespread in the Canterbury Plains, Heretaunga Plains, Manawatu Plains, Wairarapa and Hutt Valley, Marlborough, Kaikoura, and Southland (White, 2001). These aquifers are of great economic importance for water supply, as they have a high water yield and relatively uniform water storage. For example, both domestic water supplies and irrigation supplies in Canterbury are derived predominantly from alluvial gravel aquifers. Alluvial gravel aquifers are vulnerable to contamination because of their high permeability, low adsorption capacity

(with little fine material and organic matter present) and the common presence of preferential flow paths.

The alluvial gravel aquifer at Burnham in the Canterbury Plains was selected for our studies. The aquifer media can be categorised into three groups: fine material (< 2 mm, sand, silt and clay), non-coated gravels and coated gravels. The coating of the gravels, 6–13 µm in thickness, comprises predominantly Fe-oxide (> 90%, as hydrous ferric oxides) with some Mn-oxides (< 10%) associated with it (Hinton and Close, 1998). Non-coated and coated gravels, as well as fine material (\leq 2 mm) have a similar surface composition: the total surface was predominately composed of O, Si, and Al. The aquifer material had an extremely low cation exchange capacity and organic carbon content (0.04%). Table 1a shows the chemical composition of the aquifer material for the fine fraction (< 2 mm). The sorption characteristics of the fine materials and gravels (Table 1b) indicates

Table 1 – Chemical properties of the aquifer media

(a) Compositions (%) of the fine fraction (<2 mm) detected from x-ray fluorescence analysis

Aquifer media	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O	K ₂ O	CaO	MgO	TiO ₂	P ₂ O ₅	MnO	OC
Alluvial gravel ¹	70.64	13.66	3.89	3.57	2.62	1.20	0.89	0.48	0.12	0.06	0.04
Pumice sand ²	66.15	14.28	8.13	3.35	1.26	2.94	1.88	0.97	0.08	0.15	0.11*
Coastal sand ³	82.30	9.13	1.64	2.65	1.77	0.71	0.53	0.24	0.05	0.02	0.07

* total carbon content ¹Close & Pang, 1995 ²Pang *et al.*, 2004b ³Pang *et al.*, 2004c

OC - organic carbon content

(b) Adsorption characteristics of gravel aquifer media
(source: Hinton and Close, 1998)

Category	Description	CEC (cmol/kg)	SSA (m ² /g)
Coarse (> 2mm)	Non-coated gravel	0.18	1.1
	Coated gravel	0.19	1.2
Fine (< 2mm)	Sand, silt, clay	2.47	6.7

CEC - cation exchange capacity

SSA - specific surface area determined by adsorbing para-nitrophenol from xylene solution.

that the fine fraction (sand, silt and clay) of the aquifer material plays the most important role in the sorption of heavy metals, as it has a much higher cation exchange capacity and specific surface area than coated and uncoated gravel surfaces.

Pumice sand

Pumice sand aquifers are a major type of aquifer in the central North Island, in the Waikato and Bay of Plenty regions. There are also some locally distributed pumice sand aquifers in the Franklin area in Auckland (J. Hadfield pers. comm.), the flats of Poverty Bay in Gisborne (D. Gordon pers. comm.) and Ruataniwha Plains in Hawke's Bay (T. Brooks pers. comm.). In the central North Island (e.g., Rotorua District), the overlying pumice soils are often used for the disposal of domestic and industrial effluent, as they are porous and relatively permeable. In many areas, the groundwater tables are close to the surface and effluents can readily enter pumice sand aquifers to cause contamination of the underlying groundwater. Pumice sand formations often have an acidic environment, due to the presence of acidic volcanic ash in the sediments and the oxidation of sulphuric minerals in debris deposits derived from the volcanic bedrock. The acidic environment promotes the dissolution of heavy metals in the groundwater. Pang (1995) found that the groundwater of the pumice sand aquifer in the Te Aroha area contained naturally elevated levels of Fe, Mn, Pb, Cd and Cu. In a study of soil and groundwater contamination at some timber-treatment sites, Armishaw *et al.* (1994) found that the leachability of heavy metals in pumice media was high due to its acidity, and that the contamination from Cu, Cr and As was distributed as far down as the water table (1 m below ground level).

The pumice sand material used in our experiments was taken from 0.5 m below the water table during well-drilling at Hamilton.

The chemical composition of the aquifer material is given in Table 1a. Analysis of the pumice sand aquifer material showed a total carbon content of 0.11%, with an estimated allophane content of approximately 0.8%. Clay minerals were not detected and the crystalline material was made up of quartz (45%) and albite (55%). The pumice sand aquifer material had a mean cation exchange capacity of 2.49 cmol/kg.

Coastal sand

Coastal sand aquifers, with varying parent materials, are widely distributed along the coasts of New Zealand. Unlike alluvial gravel and pumice sand aquifers, coastal sand aquifers often contain peat deposits and the groundwater can sometimes be slightly acidic. On the other hand, coastal sands may contain shells and as a result the groundwater can be slightly alkaline.

The coastal sand aquifer material used in our study was obtained from a pit excavated at the coast at Woodend, North Canterbury. The chemical composition of the aquifer material is given in Table 1a. The aquifer sand contained a mean total organic carbon content of 0.066% (0.064–0.067%). Clay minerals were not detected and the crystalline material was made up of quartz (85%) and albite (15%). The shallow groundwater in the pit was acidic (pH = 4.25). However, at the same site, the groundwater pH was 7.7 in a well 25 m deep, with its water table 1.58 m below ground level. This is probably because the deep aquifer media contained some shell layers.

Experimental conditions

The experimental conditions for the field and column experiments have been described previously (Pang and Close 1999a; Pang and Close 1999b; Pang *et al.* 2002; Pang *et al.* 2004a; Pang *et al.* 2004b), and will be only briefly mentioned. The experimental conditions described below focus on the

additional batch experiments that have not been documented previously.

Batch isotherm experiments

Adsorption isotherms of Cd and Zn in the aquifer media of alluvial gravel, pumice sand and coastal sand were determined under equilibrium conditions. To approximate the natural chemical environment, native groundwater obtained from the same place as the aquifer material was used as the background solution when the solutions were spiked with a metal at different concentrations. Table 2 lists some experimental conditions for the adsorption isotherms. To mimic the bulk density and porosity of the aquifer material, a low solution-to-solid ratio (about 0.5) was used. Different pH conditions were tested in the experiments, to account for the possible pH ranges of the groundwater for specific aquifer media. The initial pH was adjusted to the desired levels using HNO₃ and NaOH. Blanks were prepared to examine mass loss through metal precipitation and adsorption to the container walls—the mass loss can be determined from the initial and final metal concentrations.

The batches were gently shaken for 18 hours at room temperature (20°C ± 1).

Samples were taken to measure initial and final metal concentrations, and the initial and final pH were measured. The mass of metal adsorbed was determined by mass balance less the amount precipitated and adsorbed to the container walls. The final solutions were filtered through a 0.45 µm membrane. The metal samples were then acidified and analysed using a Flame Atomic Absorption Spectrometer with a detection limit of 20 µg/l. To assess the effect of precipitation on metal adsorption, the kinetics of Cd precipitation were examined in the studies of Pang and Close (1999b) on groundwater in a gravel aquifer, and Pang *et al.* (2004b) on groundwater in a pumice sand aquifer. MINTEQA2 (Brown and Allison, 1987) was used to examine whether any precipitation of the metals in the ground water was likely at different metal concentrations, pH and HCO₃⁻ levels.

Column experiments

A series of column experiments was carried out under various flow rates (18–61 m/day for the alluvial gravel and 1.7–1.8 m/day for the pumice sand) and pH conditions (pH=6–8), using columns of 0.18 m length (for Cd, Zn and Pb) and 2 m length (Cd only). The

Table 2 – Experimental conditions of batch adsorption isotherms

Heavy metal	Aquifer media	Solution : solid ratio	Final pH	% precipitation in control
Cd	Gravel	80 ml: 150 g	6.0	9.9–30.6
	Gravel	80 ml: 150 g	7.0	1.4–39.6
	Pumice sand	80 ml: 140 g	6.4	5.2–11.9
	Coastal sand	40 ml: 80 g	5.0	2.8–15.0
	Coastal sand	40 ml: 80 g	6.0	5.7–22.8
	Coastal sand	40 ml: 80 g	7.0	6.2–27.6
Zn	Gravel	80 ml: 150 g	6.0	0.0–65.1
	Gravel	80 ml: 150 g	7.0	0.0–58.9
	Pumice sand	80 ml: 140 g	6.4	0.8–2.9
	Pumice sand	80 ml: 140 g	7.0	0.0–12.7
	Coastal sand	40 ml: 80 g	5.0	0.0–7.8
	Coastal sand	40 ml: 80 g	6.0	1.2–11.5
	Coastal sand	40 ml: 80 g	7.0	2.1–26.3

well-mixed aquifer material, with a particle size distribution similar to that in the field, was uniformly packed into the column under saturated conditions. A pulse of metal solution was injected into the column, followed by flushing with a metal-free solution (in most cases tap water was used). In the study of bacteria-facilitated metal transport, the bacterial solution (*Bacillus subtilis* endospores or *Escherichia coli*) was injected one hour after injection of the metal solution. A conservative tracer (Br or tritiated water) was used for each experiment to indicate flow.

Field experiment

The field experiment was conducted under a natural gradient of groundwater in an alluvial gravel aquifer at Burnham, Canterbury, immediately upgradient of a sewage plant. Ground water velocities at the site varied between 9–104 m/day, with longitudinal dispersivities ranging from 0.12–9.81 m (Pang and Close, 1999a). A pulse of solution containing Cd and rhodamine WT was injected into the injection well, two hours after the injection of a pulse solution containing *B. subtilis* endospores and *E. coli*. Samples were collected from the down-gradient wells.

Modelling approach

Batch adsorption isotherm data were fitted with a Freundlich function:

$$S = K C_{eq}^n \quad (1)$$

in which S is the adsorbed concentration at equilibrium ($\mu\text{g/g}$), C_{eq} is the dissolved concentration at equilibrium (mg/l), K is the equilibrium adsorption partition coefficient (ml/g), and n is the Freundlich exponent constant. The curve was fitted using the Solver function in Excel, with a minimised sum of squared residuals.

The constant K concept assumes that the reactions do not involve a change of

chemical species. In reality, speciation often occurs due to a change of pH and redox conditions in sites contaminated with heavy metals. Therefore, K would be constant over time and space only for systems with steady-state groundwater chemistry and would not be applicable for systems under dynamic chemical evolution (Reardon, 1981). Our choice of the constant K approach is mainly because it is commonly used in most contaminant transport models available today. In addition, metal precipitation is generally much slower than metal adsorption (Langmuir and Mahony, 1985; Fuller and Davis 1987; Holm *et al.* 1996): precipitation is often in weeks and adsorption in seconds (Langmuir and Mahony, 1985).

Data from the column experiments were analysed using a one-dimensional two-site adsorption-desorption transport model, CXTFIT (Toride *et al.*, 1995), and field experimental data were simulated using a three-dimensional two-site adsorption-desorption transport model, N3DADE (Leij and Toride, 1997). Detailed descriptions of these models were given previously (Pang and Close, 1999a, 1999b; Pang *et al.*, 2002). The model-derived parameters for describing metal adsorption include adsorption rate (day^{-1}), desorption rate (day^{-1}), and the retardation factor, R . The retardation factor is the ratio of the pore-water velocity ($V_{\text{pore-water}}$), in m/day, to the velocity of the metal movement in the groundwater (V_{metal}):

$$R = \frac{V_{\text{pore-water}}}{V_{\text{metal}}} \quad (2)$$

Adapting from Fetter (1993), the retardation factor (R) has a relationship with the adsorption coefficient (K):

$$R = 1 + \frac{\rho_b}{\theta} K n C^{n-1} \quad (3)$$

in which θ is the porosity of the aquifer media

(cm^3/cm^3) and ρ_b is the bulk density of the aquifer media (g/cm^3). When adsorption is nonlinear (i.e., $n > 1$), R is not a constant but a function of concentration. For $n < 1$, R decreases as the concentration increases, while for $n > 1$, R increases as the concentration increases. For $n = 1$, adsorption is linear and R is a constant as below:

$$R = 1 + \frac{\rho_b}{\theta} K \quad (4)$$

Results and discussion

Attenuation and transport of selected heavy metals

Equilibrium isotherms of Cd and Zn obtained from the batch adsorption experiments are shown in Figures 1 and 2, and the values of the adsorption coefficient

(K) are listed in Table 3. Table 4 summarises the retardation factors determined from the column and field experiments at different flow velocities, transport scales, metal concentrations and pH levels, as taken from Pang and Close (1999a, 1999b), and Pang *et al.* (2002, 2004a, 2004b).

Table 3 indicates that the values of the Freundlich exponent (n) are generally less than one, indicating that the adsorption of the metals to selected aquifer media is highly nonlinear and that the retardation factor (R) would decrease as the metal concentration increases. Although there are some variations in experimental results, the adsorption of the metals generally increases as pH levels rise.

We believe that the fine fraction (< 2 mm) of the gravel aquifer media plays an important

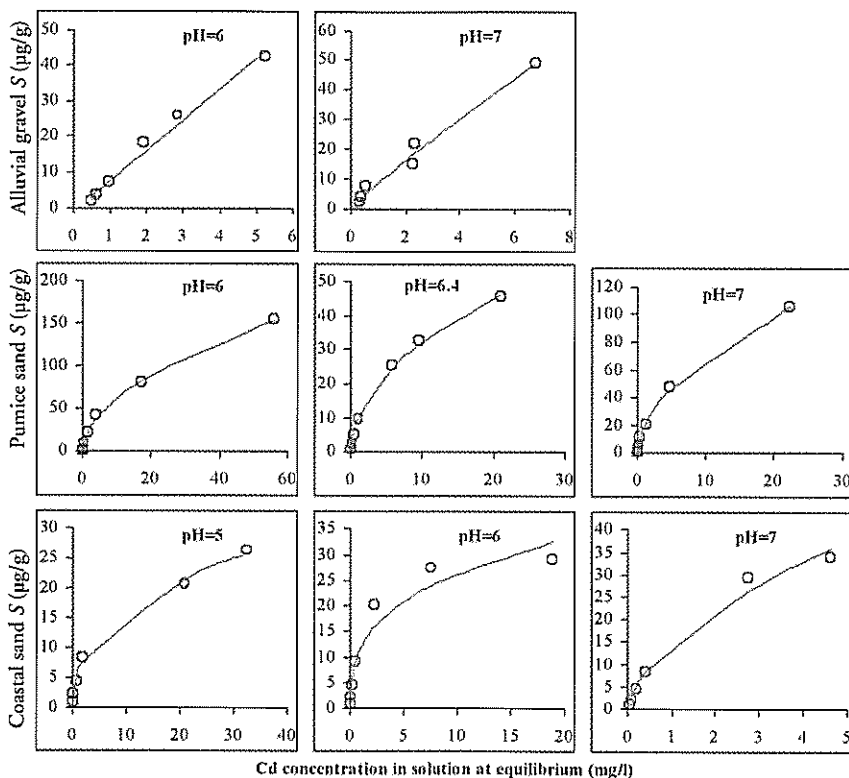


Figure 1 – Cd adsorption isotherms determined at equilibrium conditions for selected aquifer media. Circles – observed, Dashed lines – fitted with Freundlich isotherm function. pH values given are equilibrium (final) pHs.

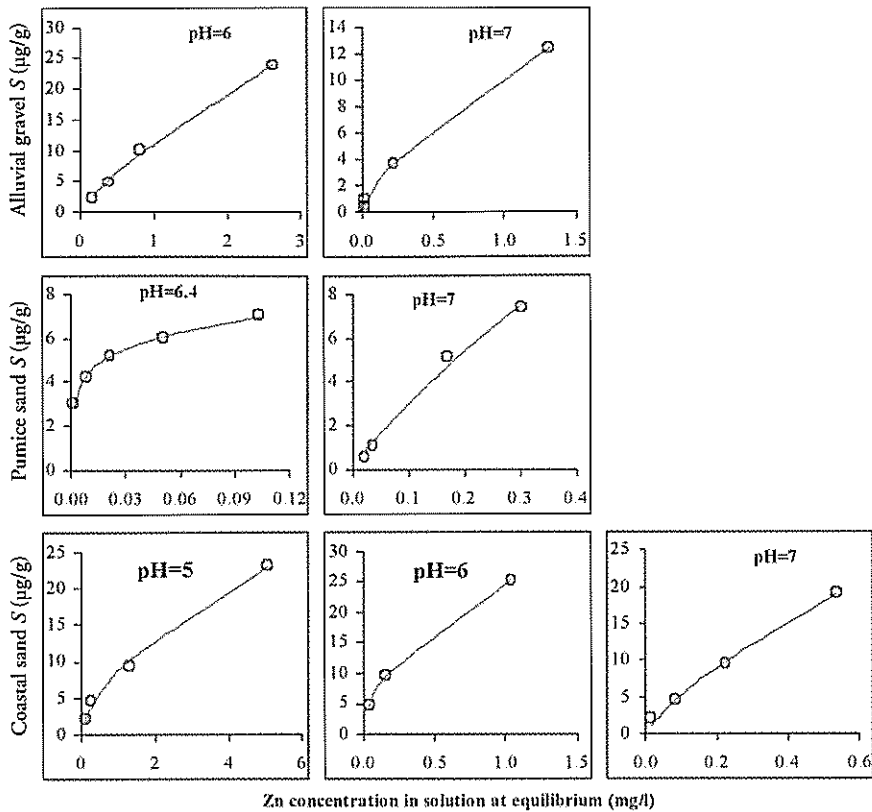


Figure 2 – Zn adsorption isotherms determined at equilibrium conditions for selected aquifer media. Circles – observed, Dashed lines – fitted with Freundlich isotherm function. pH values given are equilibrium (final) pHs.

role in the adsorption of the cationic metals investigated, as the fine material has a greater adsorption capacity than the gravel component on a weight-to-weight basis, as shown in Table 1b. Hinton (1997) found that although coated gravel does adsorb metals more efficiently than the non-coated gravel during the first 30–180 minutes of the batch tests, over longer periods of time, when the system is at equilibrium, the coated and non-coated gravel adsorb the heavy metals to the same extent. She also found that there is no significant difference in the iron content between the coated and non-coated gravels, as visible inspection suggested.

Results from the column experiments suggest that the transport characteristics of Cd and Zn were alike and that their retardation factors (R) were similar. Pb was one to two orders of magnitude more retarded than Cd or Zn. For the same aquifer media, retardation of the metals tended to increase at low flow velocities and decrease at high flow velocities. At similar flow velocities, field-determined R -values were lower than those determined from column experiments (Table 4). When metal concentrations were similar, column-determined adsorption parameter values (Table 4) seemed to be lower than those determined from batch isotherm experiments

Table 3 – Adsorption parameters determined from batch isotherm experiments

Metal	Metal concentration <i>C</i> (mg/l)	Adsorption coefficient <i>K</i> (ml/g)	Freundlich exponent (<i>n</i>)	Final pH	Reference
1. Alluvial gravel aquifer media					
Cd	0.5–5.2	7.99	1.04	6.0	This paper
Cd	0.3–6.7	9.15	0.88	7.0	This paper
Cd	0.03–4.3	16.82	0.52	7.1–7.4	Pang & Close, 1999b
Zn	0.16–2.6	11.39	0.78	6.0	This paper
Zn	0.013–1.31	10.43	0.67	7.0	This paper
2. Pumice sand aquifer media					
Cd	0.03–55.94	20.16	0.50	6.0	Pang et al. 2004b
Cd	0–21	10.40	0.49	6.4	This paper
Cd	0.05–22.34	20.12	0.54	7.0	Pang et al. 2004b
Zn	0–0.1	10.69	0.19	6.4	This paper
Zn	0.02–0.3	19.98	0.81	7.0	This paper
3. Coastal sand aquifer media					
Cd	0–32.3	6.12	0.42	5.0	This paper
Cd	0.03–0.4	16.86	0.75	6.0	This paper
Cd	0.03–4.6	12.36	0.33	6.0	This paper
Cd	2.2–18.9	18.62	0.16	6.0	This paper
Cd	0–4.6	14.59	0.59	7.0	This paper
Zn	0–0.5	8.75	0.59	5.0	This paper
Zn	0–1.0	24.91	0.50	6.0	This paper
Zn	0–0.6	30.53	0.75	7.0	This paper

Table 4 – Summary of retardation factors (*R*) determined from field and column experiments

Metal	Experiment	<i>V</i> (m/day)	<i>L</i> (m)	<i>C</i> ₀ (mg/l)	<i>R</i>	<i>K</i> (ml/g)	Final pH	Reference
1. Alluvial gravel aquifer media								
Cd	Field tracer	9–104	20–38	< 7	7–30		6.6–7.2	Pang & Close, 1999a
Cd	Column	20	2	4	133		7.8	Pang & Close, 1999b
Cd	Column	61	2	8	66		7.1–7.4	Pang & Close, 1999b
Cd	Column	18–21	0.18	4	16–39	2.16–5.36	7–7.5	Pang et al., 2003
Cd	Column	18	0.18	8	54		6.9–7.5	Pang & Close, 1999b
Cd	Column	58	0.18	9	22		7.1–7.5	Pang & Close, 1999b
Cd	Column	3–4	0.18	3	251–289		7.9–8.2	Pang et al. 2002
Cd	Column	15–18	0.18	4	40–55		7.6–8.0	Pang et al. 2002
Cd	Column	52–60	0.18	5	26–50			Pang et al. 2002
Zn	Column	4	0.18	3	158–255		7.8–7.9	Pang et al. 2002
Zn	Column	15–19	0.18	4	81–233		7.9–8.0	Pang et al. 2002
Zn	Column	45–59	0.18	4	24–32		7.6–7.9	Pang et al. 2002
Pb	Column	15–19	0.18	3	5301–5778		5.9*	Pang et al. 2002
Pb	Column	49–52	0.18	4	322–415		7.9	Pang et al. 2002
2. Pumice sand aquifer media								
Cd	Column	1.68–1.83	0.18	20	101–108	7.33–9.24	7	Pang et al. 2004b

Note:

V – flow velocity, *L* – transport scale, *C*₀ – metal concentration, *R* – retardation factor, *K* – adsorption coefficient.

*Reverse osmosis water was used to prevent precipitation of Pb.

(Table 3). The overall adsorption capacity of the selected aquifer media was similar for pumice sand and coastal sand, but less for alluvial gravel.

In the field study of Pang and Close (1999a), the Cd samples were obtained using a standard sampling technique associated with the use of a Groundfos pump. It is known that field sampling of trace metals in groundwater is very sensitive to the sampling techniques used (Creasey and Flegal, 1999; Zelewski *et al.*, 2001; Shiller, 2003), and the resultant metal concentrations are often different. In comparison with the low-flow sampling and tracer-metal clean techniques that have been developed specifically for sampling tracer metals (Creasey and Flegal, 1999; Zelewski *et al.*, 2001), the concentrations obtained using the standard sampling technique are generally higher and contain a greater degree of error. However, it is thought that the use of different sampling techniques would not change the overall pattern of the concentration breakthrough curve, rather it would change the magnitude of the concentrations. As the retardation factor is determined by the centre of the mass of the concentration breakthrough curve, the

effect of sampling techniques has little impact on the estimated retardation factors.

Using the conservative values of the retardation factors and adsorption coefficients determined in our studies, Table 5 shows a predicted range in transport distances for the different metals in the different types of aquifers. However, the wide variations in groundwater velocities and *R*-values may cause large uncertainties in predicted distances. Therefore, they are only indicative of the relative risk of metal migration in different types of aquifer. To predict particular problems, site-specific conditions (e.g., metal concentration, pH level, groundwater velocity) should be considered.

We have demonstrated that metal precipitation is a kinetic process and that it is much slower than adsorption (Pang and Close, 1999b; Pang *et al.*, 2004b). This is because the rate of nucleation and crystal growth is slow until critical super-saturation is reached, after which point the speed of precipitation rises rapidly (Schwertmann and Cornell, 1991). The MINTEQA2 simulation results suggest that for Cd concentrations at the mg/l level, some Cd would eventually form CdCO₃ complexes with HCO₃⁻ under

Table 5 – Predicted transport distances of metals in different aquifer types at typical groundwater velocities

Aquifer	V_{gw} (m/day)	Metal	<i>R</i>	<i>X</i> (m)	Note
Gravels	9–104	Cd and Zn	7–30	0.3–15 per day	V_{gw} determined from field study at Burnham, Canterbury <i>R</i> values determined from field study at Burnham. Treating Zn behave like Cd
		Pb	322–415	0.02–0.3 per day	<i>R</i> values determined from column study
Pumice sand (medium-coarse sand)	0.1–10	Cd and Zn	101–108	0.34–36 per year	<i>R</i> values determined from column study Treating Zn behave like Cd
Coastal sand (fine sand)	0.003–0.3	Cd and Zn	1.9–148	0.01–58 per year	V_{gw} reported by Slomp & van Cappellen (2004) <i>R</i> values converted from bath study results using Eq. 3 assuming porosity = 0.35, bulk density = 1.2 g/cm ³ . Treating Zn behave like Cd

the experimental conditions investigated. However, as precipitation is a slow process, the degree of metal precipitation observed was generally much lower than that at equilibrium as predicted by MINTEQA2. An exception was the experiments that were conducted over a long period of time, in which the percentage of Cd precipitated at the end of the experiment was similar to that predicted at equilibrium by MINTEQA2.

Table 2 shows that the percentage of metal precipitation observed in the batch test controls varied widely, probably because of variations in HCO_3^- concentrations and the initial pHs used in the different experiments, as well as the kinetic and heterogeneous nature of nucleation. However, we believe that metal precipitation in a batch system containing a solid was much less than that in the control (solution only). Adsorption onto solid, which occurs at a much faster rate than precipitation, would have rapidly reduced the dissolved metal concentration, with the result that the solution is not actually oversaturated with respect to the metal carbonates. Because the same percentage of metal precipitation as in the control was subtracted from a batch system containing a solid, the amount of adsorption calculated, thus the K values, may be underestimated. We consider that metal precipitation in the column experiments would not contribute to the tailing of the metal concentration breakthrough curves, and sequentially the R -values estimated, because metal carbonates are extremely insoluble and the metal precipitation would be irreversible.

Our experimental results showed that in hydrodynamic systems, metal adsorption-desorption was a reversible, kinetic process, hence the transport of metals was under non-equilibrium conditions (Pang *et al.*, 2002). Metal desorption rates were mostly two to three orders of magnitude slower than their

respective adsorption rates in both alluvial gravel (Pang *et al.*, 2002) and pumice sand (Pang *et al.*, 2004b). This resulted in significant tailing in the concentration breakthrough curves from the column and field experiments. Figure 3 gives an example of a typical Cd concentration breakthrough curve observed in a column experiment, compared with that of the conservative tracer Br. Equilibrium models, which assume adsorption/desorption is instantaneous, failed to simulate metal concentrations measured in column and field experiments, while non-equilibrium models, which consider both instantaneous and kinetic adsorption processes, accurately described metal transport behaviour under hydrodynamic conditions (Pang and Close 1999a; 1999b).

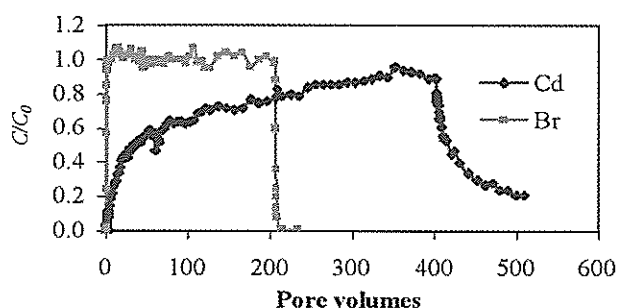


Figure 3 – A typical Cd concentration breakthrough curve from a column experiment, compared with a breakthrough curve for a conservative tracer Br.

Impacts of transport scale, reaction time and flow velocity

A comparison of Cd transport in 18-cm and 2-m long columns showed that the effect of transport scale on the transport of metals was minor (Pang and Close 1999b) for uniformly sorted and packed aquifer media. Hence, small columns could be used to obtain experimental results more quickly when aquifer materials have been well mixed

before they are packed into the columns. However, in field conditions aquifer media tend to be heterogeneous and the presence of preferential flow paths can often lead to metals moving more rapidly through aquifers. This is supported by the fact that at similar mean flow velocities, field data gave significantly lower *R*-values for Cd transport than those determined from laboratory column experiments, as mentioned previously. Therefore, when transferring laboratory-derived results to problems in the field, some safety factors should be applied to take into account aquifer heterogeneity.

As stated previously, adsorption coefficients obtained from field and column experiments were generally a few times lower than the results obtained from batch equilibrium isotherm experiments. This is because the mass exchange between adsorption and desorption did not reach equilibrium in most field and column experiments. This finding suggests that results from batch adsorption isotherm experiments should be interpreted with care when they are used to predict field problems, as the delay in the appearance of contaminants in a drinking water well or a spring could be overestimated.

We found flow velocity to be the most influential factor affecting metal non-equilibrium transport in aquifer media (Pang *et al.*, 2002). As flow velocity increased, retardation of the metal decreased, which is a typical feature of solute transport under non-equilibrium conditions. A one order-of-magnitude change in flow velocity caused a one order-of-magnitude change in the retardation factor and the adsorption rate, and a two orders-of-magnitude change in the desorption rate (Pang *et al.*, 2002). In many coastal and gravel aquifers, flow velocities vary greatly according to the season. Thus, for a particular aquifer location, there will be some temporal changes in the characteristics of metal attenuation and transport.

Bacteria/colloid-facilitated transport of metals

Our field and column experiments demonstrated that bacteria can act as carriers of heavy metals and/or facilitators of heavy metal transport in aquifers (Pang and Close, 1999a; Pang *et al.*, 2004a). Bacteria have a strong affinity towards metal ions because they are oppositely charged. Bacteria can also take part in the dissolution and formation of mineral phases. When bacteria and immobile heavy metals coexist, a portion of the total amount of the heavy metals introduced can be transported much more quickly than would be expected. This could result in two distinct peaks in a metal's concentration breakthrough curve (Pang and Close, 1999a). The early peak in the concentration breakthrough curve was narrower, and more symmetrical in shape with higher metal concentrations than the later peak, and this compared well with the shape of the bacterial concentration breakthrough curves.

In the field tracer experiment carried out in an alluvial gravel aquifer where groundwater velocity was 10–110 m/day, we observed that 5–33% of Cd was co-transported with *E. coli* and *B. subtilis* spores within a distance of 20–38 m (Pang and Close, 1999a). Taking data summarised from seven wells with facilitated transport, the transport velocity of a portion of Cd was enhanced by 5–28 times, at velocities ranging from twice as fast to six times slower than the mean groundwater velocity. The nearer the transport distance was to the contaminant source, the greater the portion of bacteria-facilitated metal transport that occurred. *B. subtilis* is a gram-positive spore-forming bacterium that is common in subsurface environments. *B. subtilis* spores are harmless to human health and are of a similar size to many bacteria, so they are often used to model bacteria in field-tracer experiments (Pang *et al.*, 1998). *E. coli* is a gram-negative species of the faecal

coliform group that is consistently present in human wastes, and hence is commonly used as an indicator of faecal bacteria.

Results from the column experiments indicate that at a flow velocity of 22 m/day and Cd input concentrations of ± 4 mg/l, bacteria-facilitated Cd transport was significant when bacterial concentrations were $\geq 10^5$ cfu/ml (Pang *et al.*, 2004a). When co-transported with the bacteria, Cd travelled 17–20 times faster than in the control experiments. Our experimental results suggest that the co-transport of metals with different bacterial species appeared to be due to different mechanisms. The co-transport of Cd with the *B. subtilis* spores was largely by adsorption. In contrast, co-transport of Cd with *E. coli* appeared to be largely by aqueous complexation, probably due to the chelation of Cd by the dissolved membrane vesicles derived from *E. coli* cell walls (Beveridge, 1999) and other dissolved organic ligands produced by *E. coli* as metabolites and exudates under the growth conditions.

A detailed batch study provided some insight into bacteria-metal interaction. We observed that the percentage of Cd-bacteria adsorption increased with increasing solution pH, bacterial concentration and negative surface charge, but decreased with increasing Cd concentration (Pang *et al.*, 2004a). The effect of cell size on metal-bacteria adsorption was not clear. Our results also show that Cd-*B. subtilis* adsorption was a kinetic, nonlinear process. There was little adsorption of Cd onto *E. coli* cells themselves, but adsorption probably took place onto their daughter products—membrane vesicles of 50–250 nm-diameter (Beveridge, 1999) and other dissolved organic ligands, which would have been filtered out by the 0.45 μ m filter paper during the sampling.

Bacteria are only one type of colloid. In the natural groundwater, colloids are abundant and include natural organic matter, clays, inorganic precipitates, fungi, algae, viruses

and metal oxides. Contaminated groundwater often contains additional man-made colloids (e.g., high molecular weight polymers, surfactants, soap residues, pulp fibers, proteins, oil droplets, detergent micelles). As with bacteria, the presence of other colloids in groundwater could also dramatically enhance the transport of immobile heavy metals. For example, in the presence of natural organic matter, Cu and Zn transport increased by 5–50 times (Karathanasis, 1999), and Pb transport increased by 10–3,000 times compared with their control treatments (Karathanasis, 2000).

Conclusions and Implications

Although groundwater contamination by heavy metals is not a common problem in New Zealand, because industrial activity here is limited, precautions should be taken when planning future land use. Our studies indicate that desorption rates of heavy metals are much slower than their adsorption rates. This suggests that once an aquifer is contaminated by heavy metals, it will take a long time to flush them from the system by natural attenuation—indeed, it could take decades to centuries based on the desorption rates that we have established.

Careful consideration of the aspects of metal non-equilibrium transport is needed for the remediation of contaminated sites, especially in designing remediation operations. Non-equilibrium transport conditions will occur if the mass-transfer times of adsorption-desorption are longer than the system's hydraulic residence times, or if surface-mediated reactions are faster than the metal adsorption-desorption processes. In general, non-equilibrium transport increases the time required for clean-up. Under non-equilibrium conditions, concentrations decrease sharply shortly after the start of the operation but decrease little afterwards.

The bacteria-facilitated metal transport

demonstrated in our studies indicates that the transport of immobile heavy metals can be dramatically enhanced in the presence of colloids. Therefore, heavy metals could arrive at drinking water wells or springs much earlier than we would expect. Colloid-facilitated transport of heavy metals increases the vulnerability of groundwater to contamination. On the other hand, this phenomenon could be utilised in the remediation of metal-contaminated sites by the introduction of desirable colloids (e.g., bacterial species, natural organic matter).

From our studies, we identified a few knowledge gaps that are worthy of future research:

- (1) Current speciation models (e.g., MINTEQA2) can predict metal precipitation only in a system containing only the solution phase at equilibrium. However, we believe that metal precipitation in a system containing both solution and solid could be different, and we observed that precipitation is a kinetic process. There is a need to develop a speciation model that considers the solid phase and also the kinetics of precipitation.
- (2) Transport models that are currently available in the literature cannot simulate colloid-facilitated metal transport. Unlike existing models that contain only two components (contaminants and aquifer media), a model that simulates colloid-facilitated metal transport needs to include three components—metal, colloid and aquifer media. Ideally, a speciation model should be incorporated into such a transport model.
- (3) Little has been reported in the literature on the risks of colloid-facilitated heavy metal transport to groundwater quality and the use of colloids to remove heavy metals from contaminated sites.
- (4) To improve removal efficiencies during remediation, more studies are needed of

the kinetics involved in the mass-transfer of adsorption-desorption, system hydraulic residence times and other surface-mediated reactions.

Lastly, we should state that the results obtained from our studies for the cationic heavy metals Cd, Zn and Pb might not be applicable for anionic heavy metals, as the transport and attenuation of anionic metals could be very different.

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