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Laboratory Based Sorption Studies to Estimate Attenuation of Contaminants in Saturated Sands

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Summary Laboratory based sorption tests (Kd-Tests) are a common means for assessment of the attenuation of contaminants in saturated sand aquifer matrix. Recent tests using three soils containing: (1) 10% fines (Soil A), (2) <5% fines (Soil B) and (3) 10% organic material (Soil C) were performed for cadmium, copper, nickel, lead, and zinc. Tests of the individual metal elements in solution showed that Soil A had a sorption capacity of <100 mg/kg for Cd, Ni and Zn, >150 mg/kg for Cu and >300 mg/kg for Pb. Soil B had a sorption capacity of <100 mg/kg for Cd, Cu, Ni, and Zn, and 110 mg/kg for Pb. Soil C had a high sorption capacity for all metals tested. Tests with all five metal elements in solution showed that Soil A had a significant reduction in sorption capacity for Cd, Ni and Zn (<20 mg/kg), and reduced sorption capacity for Pb, while Cu appeared similar. Soil B sorption capacity for Cd, Ni and Zn (<10 mg/kg) and Pb (<60 mg/kg) were also significantly reduced, while Cu appeared similar. Soil C showed sorption capacities of <160 mg/l for Cd, Ni and Zn, while Cu and Pb were still strongly sorbed. Test results indicate that Cd, Ni and Zn would be significantly more mobile in the Botany Sands aquifer than Cu and Pb. When all five elements are in solution, Cu and Pb sorb preferentially causing higher than expected Cd, Ni and Zn concentrations, allowing more rapid contaminant plume transport to greater distances. Chemical reactions associated with sorption processes were also studied as part of these tests. Results indicate that metal sorption can cause a reduction in solution pH which would enhance metal mobility. Calcite dissolution in response to lower pH conditions was also observed. Mineral dissolution can influence solution pH and increases the ionic strength of the solution, both of which play an important role in metal attenuation.

1. INTRODUCTION

The sorption properties of three sandy soils from the Eastlakes Experimental Site (ELE) were investigated using Kd-Tests (Batch Tests). The ELE site is located in the Botany Sands aquifer, Sydney, NSW. Kd-Tests are a commonly utilised laboratory based technique designed to study the sorption behaviour of solutes onto solids. Data from the test results is then used for modelling of solute transport as well as site remediation strategy development and implementation. Numerous heavy metal solute Kd-Tests are reported in scientific publications (Atanassova, 1995; Benjamin and Leckie, 1981a; Benjamin and Leckie, 1981b; Dudley et al., 1988; Fuller et al., 1996; Gerritse, 1996; Harmon et al., 1992; Kaplan et al., 1995; Loganathan et al., 1977; Madrid and Diaz-Barrientos, 1992; Mann and Ritchie, 1995; Schulthess and Huang, 1990; Zasoski and Burau, 1988), but most of these focus on specific sorption sites. Sorption site types studied included iron oxyhydroxides (Benjamin and Leckie, 1981b), carbonates (Madrid and Diaz-Barrientos, 1992), silicon and aluminium oxides (Koeppenkastrop and De Carlo, 1993; Schulthess and Huang, 1990) and hydrous manganese oxides (Loganathan et al., 1977; Zasoski and Burau, 1988). As a result data from such tests has only limited applicability to soil and water from different environments. The soils at the ELE site are likely to contain a mixture of all or most of the sorption sites described above. As a result a series of Kd-Tests using the three most common soils and simulating the groundwater environmental conditions at the ELE site were carried out.

Geological solids of all types interact with solutes in water, in a physical and/or chemical way. Kd-Tests attempt to simulate this interaction and generally consist of adding a known volume of solution which contain one or more solutes of known concentration to a known weight of a geological material and mixing them for a known time period. The solution is then separated from the solid and the concentration of solutes remaining in solution analysed. The amount of solute removed from solution is assumed to have resulted from interaction between the solid and the solution. Factors including contact time, temperature, mixing method, solid: solution ratio, absorbent moisture content, solution pH, hydrolysis and solution composition affect the results of a Kd-Test and need to be carefully considered during the planning stages of the test (Roy et al., 1991).

Kd-Test result interpretation is usually carried out by fitting theoretical mathematical model isotherms to the data. The linear, Freundlich and Langmuir isotherms are three most commonly used model isotherms. The Langmuir isotherm is the only one of the three that allows calculation of the soil sorption capacity (Roy et al., 1991). The linear and Freundlich isotherms model data where solute concentrations are too low to reach the sorption capacity of the solid. Thus when using Kd-Test results in contaminant transport models the limitations of the mathematical isotherm used need to be understood to allow realistic model development. Chemical processes involving other elements besides those solutes being studied also need to be considered when developing transport models.

2. MATERIALS AND METHODS

Standard solutions for each test were prepared using double distilled water (RO-purified with ion exchange polish, 0.2 µS/cm), and analytical grade metal salts. Sample storage and testing vessels used were made of either teflon or polyethylene.

The three most common soil types at the ELE site during previous investigations (Evans, 1993) were sampled in a test pit dug adjacent to the site. Soil A was a fine to medium grained light brown aeolian quartz sand with approximately 10% silt and clay fines with traces of organic matter. Soil B was a fine to medium grained, light yellow brown, aeolian quartz sand with traces (<5%) of silt and clay. Soil C was a fine to medium dark grey to black aeolian quartz sand with approximately 10% organic matter and traces of silt and clay fines. All three soils contained some fine shell fragment, which were observed during petrographic analysis (Evans, 1993).

Soil samples were stored in sealed polyethylene bags to preserve the field moisture content. All test sub-samples were air dried just prior to testing, to minimise any changes in soil chemistry and achieve the best possible simulation of field conditions (Roy et al., 1991; Madrid and Diaz-Barrientos, 1992). A mass of 10+/-0.01 g of soil and 20+/-0.01 ml of solution were used for each test. Samples were stored at 22°C in a climate controlled laboratory prior to and during the Kd-Tests. A blank sample using double distilled water was also added to each soil type for all Kd-Tests, to study any cation or trace metals desorption effects. A blank test without soil, using one of the standard solutions, was also included, to check potential sorption onto test vessels and equipment. A pH of 5 was planned for each solution containing the heavy metal solutes. Solution pH was adjusted where necessary using dilute HCl prior to pipetting the solution to the vessel which contained the soil sample. A tumbling wheel rotating at 20 rpm was used to mix the soil and solution for a six hour period. Earlier Kd-Tests had demonstrated that six hours was sufficient time to attain equilibrium conditions (Jankowski J, 1991). The solution pH and EC were measured prior to and after the mixing period. (Roy et al., 1991). The solution and soil were then separated by centrifuging and pipetting (Roy et al., 1991). Equilibrated solutions were stored in teflon containers and refrigerated until analytical analysis.

Standards, blanks and equilibrated solutions were analysed for boron, cadmium, calcium, copper, iron, potassium, lithium, magnesium, sodium, nickel, lead and zinc concentrations using a Perkin-Elmer Optima 3000 Inductively Coupled Plasma (ICP) spectrophotometer.

3. RESULTS AND DISCUSSION

3.1 Individual Element Test Results

Figures 1A to 1C summarise the sorption curve plots for the individual element Kd-Tests. Soil A (Figure 1A) has a sorption preference sequence as follows Pb>Cu>Cd>Zn>Ni, when the elements were individually in solution. Figure 1B shows the sorption curves for Soil B, which had a sorption preference of Pb>Cu=Cd>Zn>Ni. Soil B displayed considerably lower sorption than Soil A for all five heavy metals. Soil C showed the highest sorption (Figure 1C), for all five of the heavy metals used in the Kd-Test and showed sorption preference for Pb>Cu>Cd>Ni>Zn.

3.2 Combined Element Test Results

Figures 2A-2C summarise the results of the combined element Kd-Tests. Sorption preference of Soil A was Pb>Cu>Cd~Zn~Ni (Figure 2A), when all five heavy metals were in solution. Soil B had sorption preference of Pb>Cu>Zn>Ni>Cd (Figure 2B). Soil C showed the highest sorption of the three test soils, with sorption preference for Pb>Cu>Cd>Ni>Zn.

4. DISCUSSION

4.1 Discussion of Chemical Processes

Competitive sorption processes between heavy metals causes an overall reduction in the amount of metal solutes removed from solution, by sorption, when compared to the individual element test results. Copper sorption was the exception; the overall amount of copper removed from solution was similar in the individual and combined element tests.

An increase in the concentrations of cations as well as a reduction in solution pH were also observed with increasing metal input concentrations.

Sorption of heavy metal ions onto iron, aluminium or silicon oxyhydroxide surface sites can cause the release of hydrogen ions into solution (Benjamin and Leckie, 1981b). Benjamin and Leckie proposed the following mechanisms to explain the reduction in solution pH:

$$Me^{2+} + \underline{SOH_x} = SOMe + xH^+ \qquad (1)$$

$$Me^{2+} + H_2O + \underline{SOH_y} = SOMeOH + (y+1)H^+ \qquad (2)$$

Where

$\underline{SOH_y}$ = oxy-hydroxide sorption surface

These reaction mechanisms would result in the release of hydrogen ions into solution as metal ions sorb, resulting in the reduction of the pH.

Reduction of the pH results in increased mineral dissolution, which results in the observed increase in cation concentration with increased metal ion input. Dissolution was considered to be more likely than ion exchange as sorption of monovalent ions is preferred at lower pH and therefore a reduction in the rate of Ca concentration increase (ie non-linear trend with decreasing pH) is likely with decreasing pH (Appelo C A J, and Postma D, 1994). Shell fragments, observed during petrographic analysis (Evans, 1993), are the likely source of the calcium. Figure 3A shows an example where the observed cation increase is due only to dissolution processes resulting from the reduction of the pH. Figure 3A shows the increase in the four major cation concentrations with decreasing solution pH, which results from zinc sorption onto Soil A during the individual element test. As seen on Figure 3A the cation concentrations increase linearly with decreasing pH, indicating that dissolution is likely to be the dominant chemical process that occurs. Figure 3B shows an example where dissolution in response to lower pH can only account for part of the observed increase in cation concentration. As observed on Figure 3B, dissolution is the dominant chemical process until the pH reaches 4.2. Once the pH drops below 4.2 the rate of Ca and Mg concentration increase accelerates, while the Na increase slows significantly. This suggests that ion exchange between Na and Ca and Mg occurred. This observation appears to confirm that monovalent ions are preferred exchangers as the pH of the solution decreases. The data presented on Figure 3B was from the Soil C individual element Kd-Test with Cd in solution.

4.2 Modelling of Chemical Processes

As equilibrium conditions existed at the end of the Kd-Test mixing period, thermodynamic equilibrium modelling of the chemical processes postulated in section 4.1 was feasible. MINTEQ-2A (Allison et al., 1991) was used to simulate the sorption and mineral dissolution processes described in Section 4.1.

As sorption processes occur at a significantly faster rate than mineral dissolution (Appelo and Postma, 1994), the model was set up as follows:

a) The measured pH and solute concentrations of the standard solutions were entered into the model and the solute speciation calculated.

b) Using the modelled solute species in solution, Formula (1) was modified with the correct molar prefixes for each of the five elements used in the Kd-Tests.

c) The modified sorption reaction equations were then added to the model to simulate metal removal from solution and hydrogen ion release.

d) Finally, small amounts of calcium carbonate were dissolved stepwise by the model to simulate mineral dissolution.

Step a) model results indicated that the heavy metals speciated into a variety of mono- and divalent complexes at the start pH of 5. The metal speciation calculated by the model are summarised in Table 1.

Table 1. Metal Speciation at injection pH

Cadmium			mmol/l
44%	as	Cd^{2+}	0.208
45.10%	as	$CdCl^+$	0.213
2.70%	as	CdCl2	0.013
8%	as	$CdBr^+$	0.038
Copper			
97.60%	as	Cu^{2+}	0.867
2.20%	as	CuCl	0.019
Nickel			
96.80%	as	Ni^{2+}	0.904
2.60%	as	$NiCl^+$	0.024
Lead			
68.50%	as	Pb^{2+}	0.169
26.20%	as	$PbCl^+$	0.065
4.50%	as	$PbBr^+$	0.011
Zinc			
97.60%	as	Zn^{2+}	0.767
2.30%	as	$ZnCl^+$	0.018

Step b) The miliequivalants of charges removed and released by metal sorption were then estimated and are summarised in Table 2. Formula (1) was then modified to allow for metal speciation and entered into the model.

Step c) The modified sorption reaction equations are presented below.

$$\begin{aligned}
1.411SOH + Cd^{2+} &= S_{1.411}O_{1.411}\text{-}Cd + 1.411H^+ \\
1.974SOH + Cu^{2+} &= S_{1.974}O_{1.974}\text{-}Cu + 1.974H^+ \\
1.962SOH + Ni^{2+} &= S_{1.962}O_{1.962}\text{-}Ni + 1.962H^+ \\
1.677SOH + Pb^{2+} &= S_{1.677}O_{1.677}\text{-}Pb + 1.677H^+ \\
1.975SOH + Zn^{2+} &= S_{1.975}O_{1.975}\text{-}Zn + 1.975H^+
\end{aligned}$$

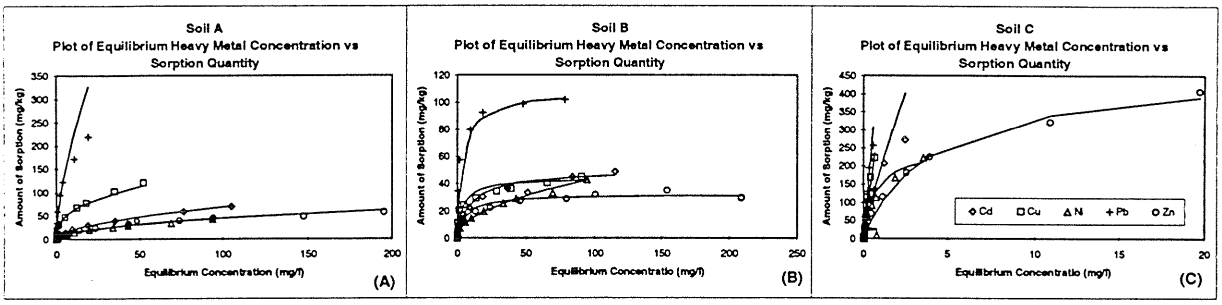

Figure 1. Sorption plots and isotherms for individual element Kd-Tests.

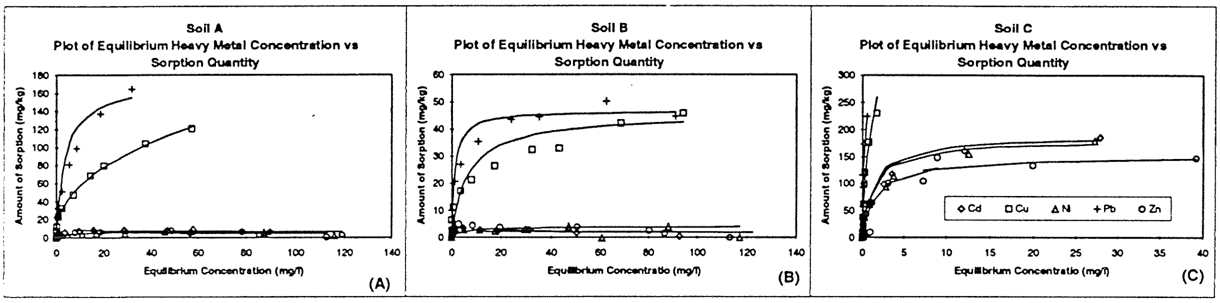

Figure 2. Sorption isotherms for combined element Kd-Tests.

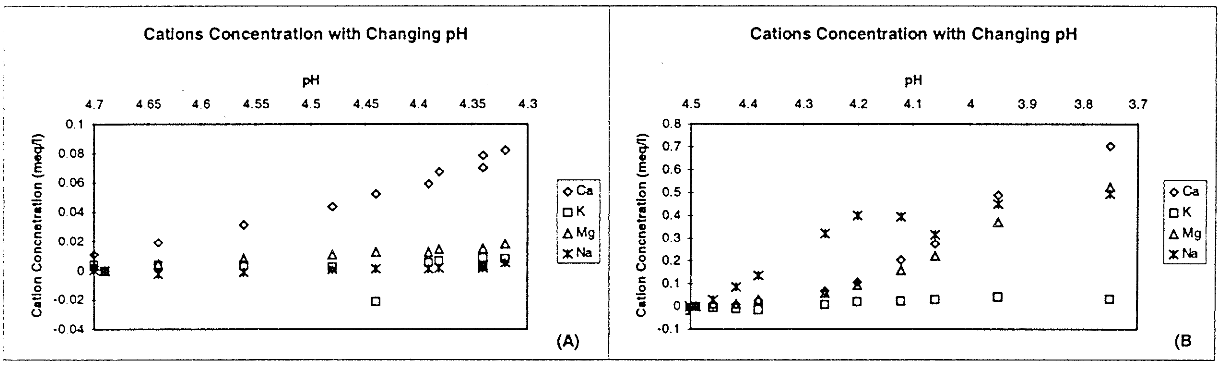

Figure 3. Changes in cation concentration with changing pH.

Once the sorption reactions were entered the model was run and the equilibrium pH calculated. The results indicated that pH values as low as 2 were feasible. Mineral dissolution, particularly of calcium carbonate, is the likely cause of the higher pH values measured during the Kd-Tests.

Step d). Small amounts of calcium carbonate were allowed to dissolve during each model run and the pH calculated. As no calcium ions were included in the solutions it can be considered as an indicator of the amount of calcium carbonate dissolved.

Thus two checks on the model performance were available. One was the estimated pH compared to the measured pH and the second was the predicted calcium concentrations compared to the actual measured concentration. The model achieved good agreement between the measured and estimated pH and calcium concentrations.

4.3 Analysis of Results

Sorption isotherms, using the linear, Freundlich and Langmuir model, were fitted to the individual and combined element Kd-Test results. Once the model with the best fit to the data was established a retardation factor and where possible soil sorption capacity were calculated. Model fitting and parameter estimation was carried out using the method outlined by Roy et al. (1991). Each of the three models was fitted to the data and the one with the highest R^2 value was used to calculate the retardation factor and where applicable the soil sorption capacity (Bowman et al., 1984). Table 2 summarises the results of the data analysis, while the models fitted to the data are presented on Figures 1A-1C and 2A-2C. The observed reduction in sorption of Cd, Ni, Pb and Zn between the individual and combined element Kd-Test results observed when comparing Figures 1A-1C with 2A-2C are also evident in Table 2. Table 2 also shows that there is no significant difference in the sorption behaviour of copper on all three soils, between the individual and combined element Kd-Tests. Retardation factors calculated for all test data show that a solution containing Ni and Zn, individually or combined, would flow at or near the groundwater flow velocity when travelling through any of the three soils used in the tests. Cd, Cu and Pb showed a tendency for retardation in Soil A and particularly Soil C, while little or no retardation could be expected in Soil B. Retardation factors for all five heavy metal ions used showed a distinct decrease between the individual and combined element Kd-Tests.

Table 2. Summary of individual and combined element Kd-Test analysis.

		Individual Elements			Combined Elements		
Element	Soil	Isotherm	Retardation Factor	Sorption Capacity	Isotherm	Retardation Factor	Sorption Capacity
Cadmium	A	Freundlich	1.048	not reached	Langmuir	1.000	7.04
Cadmium	B	Langmuir	1.000	50.25	Langmuir	1.000	1.87
Cadmium	C	Freundlich	5.990	not reached	Langmuir	1.002	131.58
Copper	A	Freundlich	1.107	not reached	Freundlich	1.112	not reached
Copper	B	Langmuir	1.001	44.05	Langmuir	1.000	45.45
Copper	C	Freundlich	30.190	not reached	Freundlich	2.506	not reached
Nickel	A	Freundlich	1.031	not reached	Langmuir	1.000	6.40
Nickel	B	Langmuir	1.000	29.85	Langmuir	1.000	0.75
Nickel	C	Langmuir	1.005	256.41	Langmuir	1.003	131.58
Lead	A	Freundlich	1.605	not reached	Langmuir	1.001	172.41
Lead	B	Langmuir	1.000	108.70	Langmuir	1.001	46.73
Lead	C	Freundlich	25.170	not reached	Langmuir	1.027	303.03
Zinc	A	Freundlich	1.033	not reached	Langmuir	1.000	4.52
Zinc	B	Langmuir	1.000	32.26	Langmuir	1.000	1.89
Zinc	C	Langmuir	1.002	476.19	Langmuir	1.002	151.52

Results of the model analysis showed that the Freundlich isotherm best fit the majority of the individual element Kd-Tests, indicating that metal ion concentrations used in the tests were not high enough to allow estimation of soil sorption capacities. For those models where the Langmuir isotherm best fit the data, the soil sorption capacities were calculated and the results are summarised on Table 2. The Langmuir isotherm best fit the data in the majority of the combined element Kd-Tests for a similar range of input concentrations. Competitive sorption processes resulted in a reduction of soil sorption capacity of up to 98% for some heavy metal solutes. In the combined element Kd-Tests soil sorption capacities could be calculated for all metal element, with the exception of copper in the Soil A and C Kd-Tests. As can be seen on Table 2, there is little difference in the sorption behaviour of copper on Soil A and B between the individual and combined element Kd-Tests.

5. CONCLUSIONS

Numerous potential sources of heavy metal contamination exist in the Botany Sands Aquifer. These include landfills (usually unlined), industrial areas (which include metal plating works) and grassland subject to fertilisation. A series of Kd-Tests using Cd, Cu, Ni, Pb and Zn metal ions in solution were undertaken to gain a better understanding of potential metal transport behaviour. The sorption behaviour of the five metals onto three different soil types was studied. Test conditions were designed to simulate the groundwater environment commonly encountered in the Botany Sands aquifer.

Individual element test results indicate that Cd, Ni and Zn would transport at or near the flow velocity of the groundwater, with sorption reducing their solution concentrations along the flow path. Soil A contains silt and clay fines, which cause some retardation of dissolved Cu and Pb ion species. Sorption rates of all five metals onto soil A were also relatively high. Soil B showed lower retardation and sorption of metal species in solution than either soil A or C, resulting in potentially greater transport distances at higher concentrations for metal ion species in solution. Soil C showed the highest retardation and sorption capacity, particularly for Cd, Cu and Pb metal ion species, of the three test soils used.

The combined metal element Kd-Tests showed significant reduction in metal species retardation. Soil sorption capacities for individual metals were also substantially reduced, with copper being the exception. Copper sorption does not appear to be influenced by competitive sorption processes, to any significant extent. This indicates that copper is either sorbed in preference to the other four metal elements or is subject to sorption onto a copper specific site. Competitive sorption processes would significantly enhance the mobility of heavy metal species in solution, particularly those of Cd, Ni and Zn.

By measuring the concentrations of other elements in solution, including the four major cations (Ca, K, Mg and Na), at the end the Kd-Tests other chemical processes were indicated. The pH of the solution was impacted by metal sorption, which released hydrogen, lowering pH and causing mineral dissolution, particularly of calcium carbonate, which raised solution pH. Modelling of these processes using the thermodynamic equilibrium model MINTEQ-2A, indicated that metal species sorption would decrease solution pH. A reduction in the pH of the solution would reduce the tendency of metals to sorb (Appelo and Postma, 1994) and therefore enhance metal mobility. The lower pH of the solution leads to the dissolution of minerals, particularly calcium carbonate. Dissolution of minerals has a twofold effect. Firstly it increases the ionic strength of the solution, which enhances metal transport (Appelo and Postma, 1994). Secondly calcium carbonate dissolution increases the pH, which results in higher sorption rates and metal species retardation(Appelo and Postma, 1994).

Traditionally Kd-Tests have been used to calculate retardation factors and soil sorption capacities (where applicable) for use in contaminant transport models. The results of the Kd-Tests described in this paper clearly demonstrate that it is important to also consider other chemical processes, geology and mineralogy of the test solids, as they can have a significant impact on the mobility of heavy metal solutes.

Based on the Kd-Test results, the sandy soils at the ELE site would preferentially sorb copper and lead from a solution containing dissolved Cd, Cu, Ni, Pb and Zn solute species. This preferential removal of Cu and Pb would significantly enhance the mobility of Cd, Ni and Zn. Similar behaviour of heavy metal solutes could be expected in other aeolian sand deposits in the Botany Basin.

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