

The BTEX retention measurements were measured similarly, although because the components are so volatile care was taken in experiment design and procedure to minimise any loss by evaporation. The results showed that the soil type had little effect on the concentration of BTEX in the water solution, except the peat, which removed most of the BTEX from solution

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1. Introduction

A very common route for the transport of contaminants from on or in soils to the wider environment and distant ecosystems is through the seepage of water through the soils and sub-soils in the unsaturated (vadose) zone into groundwater aquifers. The effects of the subsoil on the rate and distance of movement of contaminants is largely unknown for specific New Zealand soils in particular and for most subsoil types in general. It was beyond the scope of our study to carry out comprehensive and definitive measurements of the effects of all, or even a selection of, significant variables affecting the properties of the subsoils and their adsorptive capacity. Instead, we have ascertained the relative retention properties under typical conditions for important types of New Zealand subsoils.

The effectiveness of the subsoil in inhibiting contaminant migration determines to a large degree the rate and degree of contamination of the underlying groundwater. Groundwater is a principle vector for the transfer of contaminants into the wider environment and so the contaminants can affect the ecosystems in the media through which the water and groundwater move, the systems into which they discharge (springs, lakes, rivers, harbours, estuaries, wetlands, coastal zone) and the users of the groundwater, for drinking, in process industries or agricultural irrigation (see Fetter, 1993). The risks posed by contaminated sites must take these into account and this involves good understanding of the groundwater systems themselves, the transport processes through the unsaturated zone and in the saturated zone, the chemical and biological processes acting on the contaminants which will affect the transport, and the exposures of the at risk receivers.

Soils, soil media, subsoils and the vadose zone are terms that may be confused. In the following text, the term subsoil will be used to mean the soil media underlying the topsoil (which are the organic-rich O, A and B layers, if present) and the water table. It does not include the topsoil and may be considered as the C-horizon and any unconsolidated material below it. The vadose zone is the zone between the ground surface and the water table and may comprise whatever material is in that zone.

The first part of the study examined the chemical and physical processes affecting a specific range of contaminants tested in significant New Zealand subsoils and aquifers. The contaminants tested were the metals cadmium, copper, chromium, mercury, nickel, lead and zinc, plus arsenic (which is not a metal but a metalloid element: hereinafter in this report will be included under the description of “heavy metals” or even “metals” for the sake of brevity) and petrol-saturated water to determine the relative retention of BTEX (benzene, toluene, ethyl benzene and xylene).

The second part examined the hydrogeological factors, built on the New Zealand experience with the DRASTIC groundwater vulnerability assessment model (Aller *et al.*, 1987) and modified and extended the factors, weightings and methods of combinations of the factors to suit the problem being addressed (Part 2).

2. Mobility of Metal Contaminants.

2.1 Introduction

Much work has been done on the mobility of many contaminants in soils (Allan *et al.*, 1994) but much of this is of little direct use to busy consultants and officials to enable the rapid assessment of the risks of contamination incidents to downstream receivers of groundwaters which may be affected. In order to rapidly make such assessments, a series of simple experiments were designed to give information on relative retention strengths of soils for metals and BTEX. The methodology and results for the BTEX experiments are in Chapter 3.

In summary, the aim of the experimental project was to determine the relative mobility of a range of metals in the typical and/or critical New Zealand subsoils. The subsoils were selected on the basis of their significance in terms of supported populations, and at the same time providing a range of compositions. The subsoils used were:

- a basalt-derived subsoil from Auckland city;
- a loess from near Balclutha;
- a fine silt from Raupara, Marlborough;
- a peat from near Hamilton;
- volcanic ash from Wairakei;
- coarse river sand from an overbank deposit in the Hutt Valley;
- fine dune sand from Paekakariki;
- weathered greywacke subsoil from the eastern Hutt Valley hills.

The chemical compositions of the soils are given in Table 2.1. Note that because of differing techniques used for different parts of the analytical set, the results do not necessarily compare as might be expected. For instance, the peat water content is given as 87.6%, while the carbon content is 20.88%. The pre-treatment of the samples for these measurements differs and for such an extreme composition this becomes numerically but not necessarily practically significant.

2.2 Experimental Methods

Initial trials using soil columns very quickly indicated that such experiments would take too long and involve too many analyses to fit within the project budget. An account of these experiments is available from the first author, as can details about the preparation of the metal solutions used. The necessary information required by the project could be gained using simple batch experiments to calculate the distribution coefficient K_d for the metal between the aqueous and the soil phases.

The metals used in the experiments were cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), mercury (Hg), nickel (Ni), and zinc (Zn), as was arsenic (As), which is not a metal but is usually included in such listings.

Method

The moisture content of a sub-sample of each of the soils was established. It was considered that drying of the soils in an oven, even at moderate temperatures, had the potential to irreversibly amend the adsorption properties of the soil. For inter-comparison purposes equal dry weights of each soil was required, and this could be calculated using the measured moisture contents.

All soils except the peat were sieved to < 2mm before the drying then well mixed and a sub-sample taken, weighed and dried at 105 C overnight, then cooled and reweighed. The peat was quite fibrous, to the extent that this method was impractical, so a portion was dried, crushed and sieved for use in the experiments. It is acknowledged that the properties of the soil were likely to be amended by this procedure. It may have been better to put some through a blender before sieving, and to use it wet. However, the volume of the wet peat that would have been needed would have made the experimental design impractical, and the dry peat was used.

Plastic centrifuge tubes (60 ml) were acid cleaned before use. To 10 g dry weight equivalent of each soil were added tap water to make up to 20 ml total water content (including the soil water) then 10 ml of the 1000 ppm metal solution in the cleaned centrifuge tube. Blanks were run with all soils with 20 ml tap water only.

The tubes were shaken vigorously in a shaker for one hour and left for 24 hours before centrifuging. The supernatant solution was decanted and then filtered through a new 0.45 µm membrane filter into acid-cleaned or new plastic vials with 1 ml 1 M HCl.

The soil was retained in the tubes and tap water added to make the total water content 30 ml, shaken as above for 1 hour, left for 24 hours and the extraction repeated as above. This enabled the measurement of the desorption coefficients.

The supernatant solutions were analysed by Spectrachem Analytical of Lower Hutt by evaporation on cellulose pads and X-ray fluorescence analysis of the pads.

Several experiments were repeated, as checks on the repeatability of the measurements. The standards were analysed by the same method.

2.3 Experimental Results

The calculated K_d values for all the batch experiments are listed in Table 2.2. K_d is defined as the ratio of the metal concentration in the solid phase (soil) to that in the liquid phase (solution) and as such, the higher the value the more strongly it is bound to the soil. Conversely, low values indicate that more of the metal is in the solution – equal concentrations (in terms of mass/mass, rather than mass/volume) will give K_d values of unity (1).

K_{d1} and K_{d2} are the values calculated from the absorption and the desorption experiments respectively. In simple systems these should be equal but soils are not simple. In almost

all measurements the K_{d2} values are higher, and in most cases, much higher, than the K_{d1} values, which is to be expected if the mechanism of metal removal from solution changes with time, e.g. from surface absorption to chemical precipitation. There are a number of such mechanisms and it is beyond the scope of this study to analyse these further.

Some results are negative and this is impossible. They occur only for the weathered greywacke subsoil, and for two elements (Cd and Hg), and may result from analytical errors. For these two elements in particular, the XRF technique is less sensitive.

One set of K_d values in particular is very high, and the calculated values are expressed as > (greater than) values. These are all for lead (Pb) and occur because its concentration in the liquid phase was below detection. In other words, the Pb in these soils is very strongly absorbed.

The absorptions of the metals follow some common patterns, with As, Cd, Ni and Zn being relatively weakly retained on all soils. Most K_d values being less than 100. Cr and Pb are the most strongly absorbed, lead particularly so.

Of the soils, the silt, peat, ash, and surprisingly, the dune sand absorb most metals the strongest. The weakest absorber is the weathered greywacke subsoil, followed by the basalt soil and the loess. These findings are also surprising, in that the presence of appreciable amounts of clay is usually considered to promote absorption, and these would be expected in each of these soils.

The K_{d2} is much greater than the K_{d1} values for Cr and Pb in silt and dune sand.

2.4 Discussion

The experimental conditions under which the measurements were carried out are quite unlike natural conditions as soils are rarely in such intimate contact with contaminant solutions and the solutions are likely to be mixtures and of quite different compositions in terms of parameters such as pH, and salinity,. The soils themselves are never uniform in size and cohesion, and no other soil from the ones used will have the same properties. Extraneous factors such as preferential flow paths, wetness, rainfall or other flushing, will affect rate of transport.

The aim of the measurements reported here are to indicate relative rates of binding of the investigated metals to different types of soils. To this end the table of calculated K_d values has been translated into the descriptors for relative mobilities (an inverse function of K_d) in Table 3.7 and 3.8. The descriptors are:

- Very high for K_d values < 10
- High for K_d values 10 < 100
- Medium for K_d values 100 < 1000
- Low for K_d values > 1000

Soil Identifier	Soil Description	Arsenic		Cadmium		Chromium		Copper		Mercury		Nickel		Lead		Zinc	
		K _{d1}	K _{d2}														
ENV98-335	Auckland Basalt repeat	14.4	48.5	19.6	25.4	56.5		64.3	330.3	114.6	1305.8	13.0	37.4	217.1	528.9	12.7	48.9
ENV98-347	Balclutha Loess repeat	3.0	10.0	5.4	33.9	59.7	1997.7	10.3	52.4	2.1	8.3	11.1	53.4	428.4	532.5	5.5	26.1
ENV98-348	Wairau Silt repeat	1.4	7.8	6.2	51.3	36.8	1162.6	19.6	141.5	11.8	282.4	10.4	62.2	>10000	1538*	5.7	46.8
ENV98-350	Waikato Peat repeat	7.3	6.1	28.1		69.5	601.3	325.4	647.8	159.8	1579.0	62.0	113.3	3591.7	2152.0	19.8	43.8
ENV98-351	Taupo Ash repeat	4.9	10.2	3.9	19.7	15.8	362.4	13.4	56.3	2.8		6.6	19.6	>10000	3592*	4.9	14.5
ENV98-352	Hutt River Sand repeat	1.1	7.6	2.0	11.9	4.1	256.8	3.8	52.4	0.7	9.3	4.0	23.6	114.2	10505.0	1.9	16.4
ENV98-353	Paekakariki Dune Sand repeat repeat	1.0	7.0	1.9	17.7	4.7	1533.2	4.3	118.5	0.7	5.9	2.9	22.8	715.9	5366.5	1.9	18.9
ENV98-349	Weathered greywacke repeat	2.2	10.2	-0.6	-8.6	6.1	95.0	1.5	8.5	-0.3	-5.0	0.8	2.0	10.9	189.3	0.9	2.1

Table 2.2 Kd Values for metal in solution in contact with soils

K_{d1} is the distribution coefficient for the adsorption measurement and is $[M_{soil}]/[M_{solution}]$

K_{d2} is the distribution coefficient for the subsequent desorption measurement

It is important to note that these are relative descriptors only and variations in any conditions may change the relativities. They are intended for guidance only. Note also that the ranges differ by factors of ten.

Changes in the chemical environment (especially pH and redox conditions) may result in very different relative mobilities for the components – acidic and/or reducing conditions will increase dramatically the mobilities of the metals. More acidic solutions will induce increased mobility of metallic species in solution, by a factor of 10 for every unit pH reduction. Reducing conditions can render metals with more than one valance state more soluble – particularly iron and manganese, which, as the oxyhydroxides have a tendency to absorb metals from solution. The peat in the experiments tends to retain the metals (except As) relative to other soils, and is reducing. The competing effects of a number of absorbing mechanisms have to be taken into account as reducing conditions and the potential higher mobilities will be countered by the availability of strongly complexing organic species binding the metals to the substrate.

Table 2.3 RELATIVE MOBILITIES FROM FRESH SPILLS

Soil\ Metal	Arsenic	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Basalt Soil	High	High	High	High	Medium	High	Medium	High
Loess	Very high	Very high	High	High	Very high	High	Medium	Very high
Silt	Very high	Very high	Medium	High	High	High	Low	Very high
Peat	Very high	High	Medium	Medium	Medium	High	Low	High
Ash	Very high	Very high	High	High	Very high	Very high	Low	Very high
River Sand	Very high	Medium	Very high					
Dune Sand	Very high	Medium	Very high					
Weathered Greywacke	High	Very high	Very high	Very High	Very high	Very high	High	Very high

Table 2.4 RELATIVE MOBILITIES FROM OLDER SPILLS

Soil\ Metal	Arsenic	Cadmium	Chromium	Copper	Mercury	Nickel	Lead	Zinc
Basalt Soil	High	High	Medium	Medium	High	High	Medium	High
Loess	High	High	Low	High	Very high	High	Medium	High
Silt	Very high	High	Medium	Medium	Medium	High	Low	High
Peat	Very high	High	Medium	Medium	Low	Medium	Low	High
Ash	High	High	Medium	High	Very high	High	Low	High
River Sand	Very high	High	Medium	High	Very high	High	Low	High
Dune Sand	Very high	High	Low	Medium	Very high	High	Low	High
Weathered Greywacke	High	Very high	High	High	Very high	Very high	Medium	Very high

3. BTEX adsorption.

BTEX (**B**enzene, **T**oluene, **E**thyl Benzene and **X**ylene) are major components of petrol, which is a common soil and water contaminant. The concentrations of these components in waters in the subsoil and aquifer materials following a petrol spill on the ground is important for assessing the risks of transport of the components to and by groundwater, quite apart from the “floating” undissolved phase (free product).

3.1 Analytical methods

The major concern with the volatile components was to avoid evaporative losses during transfer to reaction vessels and before analysis. This was accomplished by having a petrol/water mix in a separating funnel with a hypodermic syringe attached to the outlet valve. 10g dry weight equivalent of the wet soils was added to 30 ml vials which had lids with septa. These vials were evacuated with a vacuum pump through another needle, and filled with the petrol-saturated water from the separating funnel. The valve and needle were flushed with water before entry into the vial. Once almost full, the lid of the vial was just loosened so that excess saturated-water flushed through to ensure no air pockets remained.

Control samples were obtained in exactly the same way but no soil was added to the receiving vials.

The tubes were shaken and taken to the ESR laboratories for analysis within 24 hours. Biological degradation of the components is potentially significant in soils. The method of analysis was by purge trap gas chromatography.

3.2 Results

The results are listed in Table 3.1.

Immediately apparent is that the two control samples gave quite different concentrations from each other, and these values are more or less the same as for all of the samples in contact with the soils, except the peat, which absorbed most of all components. A set of K_d values has been calculated and is presented in Table 3.2. The two control samples gave quite different concentrations. If the assumption is made that the higher concentration control is the more correct, on the grounds that volatiles are more easily lost than gained, K_d values can be calculated for most components. Some soils and components gave zero or negative values, suggesting that the control also had lost volatiles before analysis. The calculated values must therefore be treated with extreme caution and are likely to be minimum values.

	Benzene mg/l	Toluene mg/l	Ethyl Benzene mg/l	<i>m+p</i> -xylene mg/l	<i>o</i> -xylene mg/l
Basalt	52	32	1.3	5.2	2.5
Loess	53	50	2.2	9.3	4.5
Silt	70	59	2.5	10	5.0
Weathered Greywacke	47	47	2.1	9.0	4.4
Peat	6.2	3.7	0.09	0.4	0.2
Ash	57	45	2.0	8.7	4.2
Alluvial Sand	64	59	2.7	11	5.6
Dune sand	55	43	1.7	8.8	4.2
Control #1	64	52	2.5	11	5.1
Control #2	47	37	1.7	7.6	3.7

Table 3.1 Analysed concentration of BTEX components in contact with soils.

	Benzene	Toluene	Ethyl Benzene	<i>m+p</i> -xylene	<i>o</i> -xylene
Basalt	0.19	0.38	0.48	0.53	0.51
Loess	0.17	0.04	0.12	0.15	0.12
Silt	<	<	0.00	0.09	0.02
Weathered Greywacke	0.27	0.10	0.16	0.18	0.14
Peat	0.90	0.93	0.96	0.96	0.96
Ash	0.11	0.13	0.20	0.21	0.18
Alluvial Sand	<	<	<	<	<
Dune sand	0.14	0.17	0.32	0.20	0.18

Table 3.2 Kd values for BTEX components in contact with soils.
The highest control concentration was used for the calculation.
< - calculated values of 0 or less.

3.3 Discussion

If these results are to be treated in the same way as the metals, then all the BTEX

components must be regarded as having very high mobility in all soils except in peat – and by extension, any subsoil which has a high organic content, in which the mobility must be regarded as low.

Generally all components have similar K_d values for each soil, with perhaps benzene being the most weakly adsorbed, except in the loess and the weathered greywacke, where it is the most strongly adsorbed.

4. References

Allan, H.E., Chin, P.H., Bailey, G.W. and Bowers, A.R.(eds)1994. Metal speciation and contamination of soil. CRC Press Inc, Boca Raton.