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**TRANSPORT PROPERTIES OF
RADIONUCLIDES AND HAZARDOUS
CHEMICAL SPECIES IN SOILS AT THE
IDAHO CHEMICAL PROCESSING PLANT**

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ABSTRACT

Near-surface, on-site disposal is being evaluated as a no-action alternative for future environmental documentation for high-level radioactive waste (HLW) stored at the Idaho Chemical Processing Plant (ICPP). As part of this evaluation, a three-dimensional code, TRACR3D, is being used to model potential transport of radioactive and hazardous species from the calcine to the Snake River Plain Aquifer under various water-contact scenarios. Laboratory studies have been completed to provide measured transport parameters for selected radionuclides and hazardous chemical species to allow for the development of accurate solute transport models.

Retardation factors (R) and dispersion coefficients for technetium (as pertechnetate, TcO_4^-) and selenium (as selenate, SeO_4^{2-}) were measured in water-saturated soil columns of alluvial (near-surface) and interbed sediments and crushed basalt. A retardation factor was also determined for selenite (SeO_3^{2-}) in basalt. The data indicated no retardation ($R=1$) of pertechnetate and selenate in all the materials studied and a slight retardation of selenite in basalt ($R=1.7$). Retardation factors for selenite in alluvium and interbed sediment were calculated from batch sorption data and were estimated to be in the range of 13-230.

Distribution coefficients (K_d) for cadmium, mercury, selenium (as SeO_3^{2-}), and strontium were measured using batch equilibrium sorption methods. Measured distribution coefficients for the sorption of cadmium and strontium on sedimentary materials were very nearly independent of initial metal concentrations in contrast to mercury and selenium whose K_d values were highly dependent on initial metal concentrations. Distribution coefficient ranges in units of mL/g were as follows: alluvium, Cd 2864-4891, Hg 236-1912, Se 5.8-63, Sr 35-52; interbed sediment, Cd 8622-10,115, Hg 72-673, Se 4.9-17, Sr 110-186; basalt, Cd 785-2319, Hg 9.2-87, Se 0.29-3.4, Sr 1.1-2.7.

SUMMARY

The disposal of calcined high-level radioactive waste (HLW) in a near-surface facility at the Idaho Chemical Processing Plant (ICPP) is being evaluated as a no-action alternative for future environmental documentation. The hypothetical transport of radioactive and hazardous constituents from the calcine through the unsaturated vadose zone and to the aquifer beneath the ICPP is being modeled. The principal transport mechanism is considered to be rainwater recharge contacting the calcine and migrating to the aquifer. Hydrogeological data for the ICPP is being assimilated, and a code called TRACR3D is being used to develop three-dimensional transport models for radioactive and hazardous chemical species. Current solute transport models have been developed based on assumed transport parameters. The purpose of the laboratory studies is to provide measured transport parameters for selected radionuclides and hazardous chemical constituents of the calcine so that more accurate transport models can be developed.

Preliminary modeling studies have indicated that technetium-99 (2×10^4 yr half life) and selenium-79 (6.5×10^4 yr half life) present in the HLW have the potential of migrating through the vadose zone and reaching the aquifer within 10,000 years should water contact occur. The modeling studies assumed no retardation in the vadose zone. In order to test this assumption, retardation factors (solvent velocity/solute velocity) for technetium (as TcO_4^-) and selenium (as SeO_4^{2-} and SeO_3^{2-}) were measured using tracer solutions and water-saturated soil columns made up of alluvium, interbed sediment and basalt. The alluvium was taken from the Fuel Process Restoration (FPR) construction pit at a depth of about 12 m below land surface. The interbed sediment and basalt were taken from depths of 35 m and 40 m respectively, and come from the same ICPP core drilling taken by the United States Geological Survey (USGS). Aquifer water and perched water obtained from a well at a depth of 38 m were used for the tests. A one-dimensional, convective-dispersive, solute-transport equation, was fitted to column effluent data using a non-linear, least-squares fitting routine. The data indicated no retardation ($R=1$) of the pertechnetate ion (TcO_4^-) and selenate ion (SeO_4^{2-}) and

a slight retardation ($R=1.7$) of the selenite ion (SeO_3^-) in basalt. A significant retardation of SeO_3^- in the alluvial and interbed sediments was observed, but a retardation factor could not be determined because the solute residence times required to measure a retardation factor were impractically long. Retardation factors for selenite were calculated from distribution coefficients obtained from batch sorption methods and were estimated to be in the range of 13-230.

Because the migration rates of cadmium, mercury, selenite and strontium were expected to be very slow in soil columns, retardation factors were estimated from distribution coefficients determined by the batch equilibrium sorption method. This method involved adding a metal tracer solution to a weighed amount of soil and determining the amount of sorbed metal by measuring the activity remaining in solution at equilibrium.

Isothermal solute sorption can generally be described by the following equilibrium expression:

$$S_m = k C_e^n \quad (\text{S.1})$$

where,

S_m = moles of solute sorbed/g of soil

C_e = equilibrium solute concentration, moles/liter

and k and n are constants. For linear sorption, $n=1$ and k is equivalent to the distribution coefficient (K_d):

$$K_d = \frac{S_m}{C_e} \quad (\text{S.2})$$

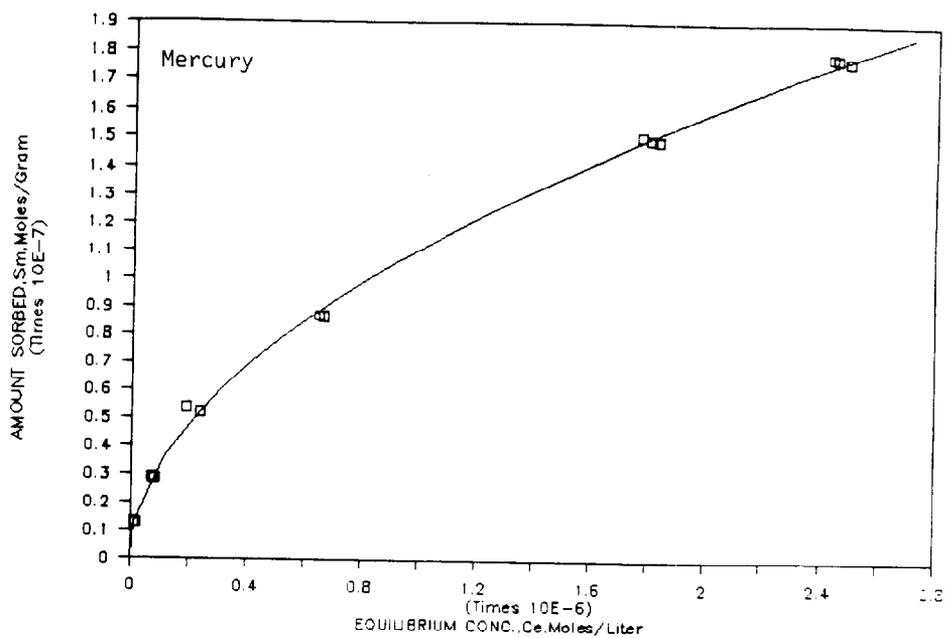
Equation (S.1), which is the Freundlich isotherm equation, was fitted to the measured data points (S_m and C_e) by first taking the natural logarithm of both sides of the equation and performing a linear regression

to obtain the constants k and n . Values for S_m were then calculated for a range of C_e values in order to construct the isotherm. The isotherms indicated that sorption of cadmium and strontium on alluvium and interbed sediment was approximately linear while sorption of mercury and selenium was non-linear. Equation (S.1) could not be fitted to the sorption data for basalt. Isotherms for the sorption of mercury and strontium on interbed sediment are illustrated in Figure S-1. The symbols shown in the plots are the measured data points in groups of three representing replicate determinations. Due to scale constraints and the close proximity of the measured data points at the lower end of the isotherms, these data points tended to be superimposed on one another.

Table S.1 summarizes the data for the sorption of cadmium, mercury, selenium and strontium on alluvium, interbed sediment and basalt. Cadmium was strongly sorbed on all the materials studied as evidenced by very large K_d values. Mercury sorption was large on alluvium and interbed sediment and moderate on basalt. Selenium sorption was low on the interbed sediment and very low on basalt. Selenium was moderately sorbed on alluvium at the lower end of the initial metal concentration range. Strontium sorption was large on the interbed sediment, moderate on alluvium and very low on basalt. The non-linear sorption characteristics of mercury and selenium are indicated in the table by the considerable dependence of their distribution coefficients (K_d) on initial metal concentrations. This dependence will have to be taken into account when developing transport models for these species.

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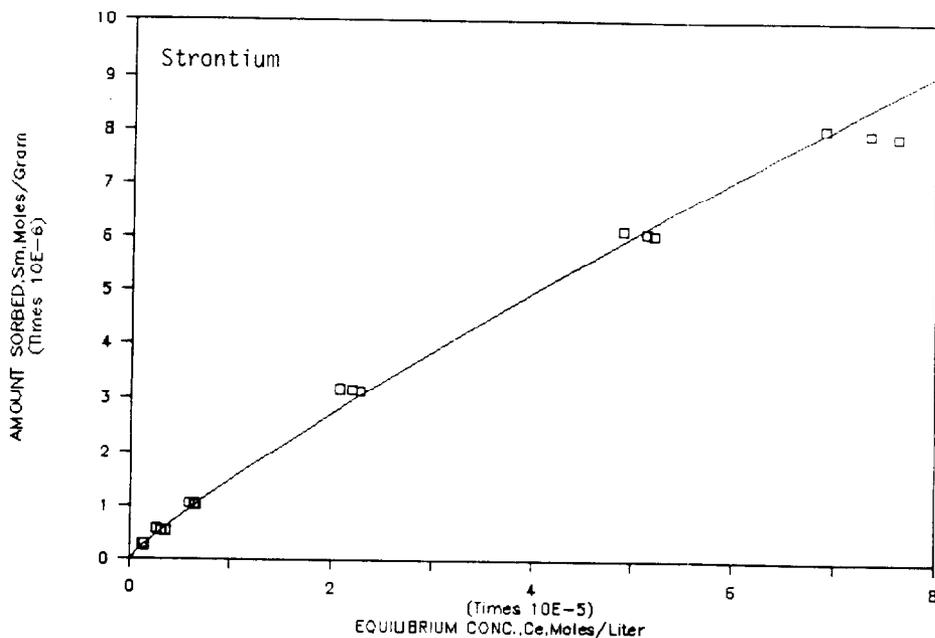


Figure S-1. Isotherms for the Sorption of Mercury and Strontium on Interbed Sediment

Table S.1

Summary of Data from Batch Equilibrium Sorption Tests

Geologic Material	Metal	Initial Concentration Range, M	Measured Kd Range (mL/g)	k (mL/g)	n
Interbed Sediment	Cd	3.7×10^{-9} - 1.5×10^{-6}	10,115-8622	1000	0.89
	Hg	6.5×10^{-7} - 1.0×10^{-5}	673-72	0.148	0.52
	Se ^a	3.5×10^{-6} - 6.6×10^{-5}	17-4.9	0.165	0.65
	Sr	1.5×10^{-5} - 4.8×10^{-4}	186-110	32.7	0.87
Alluvium	Cd	3.7×10^{-9} - 1.5×10^{-6}	4891-2864	1177	0.95
	Hg	3.3×10^{-7} - 1.0×10^{-5}	1912-236	1.89	0.64
	Se	8.6×10^{-7} - 6.6×10^{-5}	63-5.8	0.096	0.60
	Sr	7.7×10^{-6} - 4.8×10^{-4}	52-35	17	0.91
Basalt	Cd	3.7×10^{-9} - 1.5×10^{-6}	2319-785	b	b
	Hg	6.9×10^{-7} - 1.0×10^{-5}	87-9.2	"	"
	Se ^c	4.3×10^{-7}	3.4	n.d.	n.d.
		6.6×10^{-5}	0.29	"	"
	Sr ^c	7.6×10^{-6}	2.7	"	"
4.8×10^{-4}		1.1	"	"	

^a Se as SeO_3^- .

^b k and n not listed due to poor fits of equation (S.1) to data.

^c Due to very low sorption, only high and low initial metal concentrations were used. No isotherms were plotted.

n.d. = Not determined.

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I. INTRODUCTION

1. BACKGROUND

High-level radioactive waste (HLW) calcine from the reprocessing of defense nuclear fuels is generated and stored at the Idaho Chemical Processing Plant (ICPP). Disposal of the HLW in a near-surface facility onsite is being evaluated as a no-action alternative for future environmental documentation.¹ Part of the evaluation involves determining the potential for the transport of radioactive and hazardous constituents from the calcine to the aquifer below the ICPP.

The ICPP is located at the Idaho National Engineering Laboratory (INEL) in southeastern Idaho on the Snake River Plain. The Snake River Plain is a semiarid structural basin underlain by an unsaturated vadose zone which has an oxic environment and consists of a sequence of basaltic flows and interbedded sedimentary layers. The vadose zone beneath the ICPP extends to approximately 140 meters below land surface. Beneath the vadose zone lies a vast groundwater reservoir called the Snake River Plain Aquifer. A modeling code called TRACR3D has been used to develop three-dimensional models for the transport of radioactive and hazardous chemical species through the vadose zone and to the aquifer.² These models have used assumed transport parameters for the individual species. The purpose of the laboratory studies is to provide measured transport parameters for the development of more accurate transport models. This report will describe laboratory methods for measuring retardation factors, dispersion coefficients, and distribution coefficients of radioactive and hazardous chemical species using soil column and batch equilibrium sorption techniques. Distribution coefficients are used to calculate retardation factors which are used in species transport models. The geologic materials used in the study include alluvium (near-surface) and interbed sediment and crushed basalt. Since the actual basaltic layers are largely monolithic, the data for crushed basalt is presented as a comparison and may not be useful in developing transport models.

2. RADIONUCLIDES AND CHEMICAL SPECIES STUDIED

Literature surveys have indicated that technetium-99 (2×10^5 yr half life) and selenium-79 (6.5×10^4 yr half life) in the HLW may not be retarded in the vadose zone should they be leached from calcine.^{3,4} In an oxidizing environment and a groundwater at pH 8, technetium would most likely leach from the calcine as the pertechnetate ion (TcO_4^-). Equilibrium calculations and Eh-pH diagrams⁵ indicate that selenium would exist as either the selenate ion (SeO_4^{2-}) or the selenite ion (SeO_3^{2-}). Retardation factors and dispersion coefficients for selenium and technetium were determined using soil column techniques since column residence times were expected to be short. Selenium as SeO_3^{2-} was also studied by the batch equilibrium sorption method.

Cadmium and mercury are non-radioactive components of the calcine. Cadmium is used as a neutron poison in the Fluorinel Dissolution Process (FDP) and is present in calcine generated from FDP HLW. The presence of mercury in the calcine is due primarily to its use as a catalyst in the dissolution of aluminum fuels. Strontium exists in the calcine as strontium-90 (30 yr half life) which is a fission product. Should cadmium be leached from the calcine by groundwater, its solubility would probably be limited to about 1×10^{-6} M by precipitation of CdCO_3 . The predominant specie in solution would be the uncomplexed ion (Cd^{++}).⁶ Mercury solubility would be limited to about 1×10^{-4} M due to the precipitation of HgO , with the predominant specie in solution being $\text{Hg}(\text{OH})_2$ due to hydrolysis of the mercuric ion.⁷ Some precipitation of mercury as HgCO_3 may also occur. The solubility of strontium in groundwater may be limited by the solubility of SrCO_3 . Solubility calculations based on estimates of the carbonate concentration in groundwater have indicated a strontium solubility limit of 1×10^{-3} M.

Preliminary tests of the sorption properties of cadmium, mercury and strontium on alluvium indicated extensive sorption for these species. A large sorption would result in long column residence times making the use

of soil columns impractical. Hence the batch equilibrium sorption method was used to determine distribution coefficients (K_d) which can be used to estimate retardation factors for use in transport models. Although selenium sorption on alluvium was not extensive, it was also included in the batch sorption tests since previous soil column studies indicated that sorption could be significant.

II. GEOLOGIC MATERIALS AND GROUNDWATER

1. GEOLOGIC MATERIALS CHARACTERIZATION

The geologic materials used in the laboratory tests were alluvium, interbed sediment and basalt. The alluvium sample was taken from the Fuel Process Restoration (FPR) construction pit at a depth of about 12 m below land surface. The texture of the material, as determined by the United States Department of Agriculture (USDA) size classification method⁸ is a sandy loam. The interbed sediment and basalt are core materials obtained during the drilling of United States Geological Survey (USGS) perched water monitoring well number two (PW2) located immediately south of the Fuel Storage Basin (CPP-603) at ICPP. The interbed sediment was taken from the top part of the first interbed at a depth of 35 m below land surface. It consists of large, hard agglomerates which showed evidence of possible cementation and required considerable crushing resulting in particle sizes characteristic of a silty texture. The basalt was taken from below the first interbed at a depth of 40 m below land surface. It is vesicular in nature, the vesicles containing very little sediment. Table 2.1 lists the analytical data for the geologic materials. The data indicate that alluvial and interbed sediments are chemically similar and mineralogically identical with regard to the major minerals present. The iron present in the materials may be present as amorphous iron oxides since no iron-containing minerals were detected by X-ray diffraction. Due to the considerable crushing of the interbed sediment during sample preparation, the particle size distribution listed may not be representative of the sediment in its natural state. The basalt consists primarily of plagioclase feldspar. Although calcite is not generally part of the crystalline structure of the basalt it is often found in vesicles and on the surface. No iron-containing minerals were identified to account for the large weight percent of iron present. As in the alluvial and interbed sediments, the iron may be part of amorphous structures.

Table 2.1

Analytical Data for Geologic Materials Characterization

	<u>Alluvium</u>	<u>Interbed</u>	<u>Basalt</u>
CaCO ₃ , wt %	5.6	7.8	n.d.
Ca, wt %	3.3	4.9	6.2
Mg, wt %	1.0	1.7	3.6
Fe, wt %	2.5	3.7	10.0
Particle Density, g/cm ³	2.22	1.72	2.91
Particle Size Distribution, % ^a			n.a.
Sand (0.05-2.0 mm)	65.6	0.90	
Silt (0.002-0.05 mm)	22.0	87	
Clay (<0.002 mm)	12.4	11.9	
Texture	Sandy Loam	Silt	n.a.
Major Minerals	α -quartz ^b	α -quartz	Anorthite ^c
(X-Ray Diffraction Analysis)	Calcite ^d	Calcite	Albite ^e
	Albite	Albite	

^a U.S. Department of Agriculture (USDA) classification system.

^b SiO₂

^c CaAl₂Si₂O₈, a plagioclase feldspar

^d CaCO₃

^e NaAlSi₃O₈, a plagioclase feldspar

n.d. = none detected

n.a. = no analysis

All analyses were performed on crushed materials which were passed through a 2 mm sieve. Calcium, magnesium and iron analyses were performed by atomic absorption methods. Sample preparation was done by lithium tetraborate fusion followed by dissolution in dilute nitric acid.

Particle densities were determined by the mercury displacement method and particle size measurements were done by determination of particle settling rates using the pipette method.⁹ Calcium carbonate was determined by dissolving the soil in acid and coulometrically measuring the evolved CO₂.

2. GROUNDWATER ANALYSIS

The chemical composition of the groundwaters used in the soil column and batch equilibrium sorption studies is listed in Table 2.2. Groundwater W78 was perched water from the vadose zone taken at a depth of 38 m below land surface from USGS well #78. This well is located south of the Test Reactor Area (TRA) near the Big Lost River. The water is considered to be direct recharge from the Big Lost River. Groundwater W78 was used only for the soil column experiments with the alluvial sediment. Groundwater W19 was aquifer water taken at a depth of 140 m from USGS well #19 located west of TRA. The data indicate that both groundwaters are very similar in chemical composition and thus for testing purposes, aquifer water can be used to simulate water percolating through the vadose zone. Both groundwaters are buffered by a carbonate/bicarbonate system and have an average pH of 8. Oxygen analyses have indicated that the groundwaters are saturated with oxygen thus creating oxic (oxidizing) conditions. The chemical composition of rainwater recharge is assumed to reach equilibrium in the vadose zone and be similar to the groundwater used in the present study.

Cations were analyzed by atomic absorption spectrometry and anions, with the exception of HCO₃⁻ which was done by potentiometric titration, were analyzed by anion chromatography. A portable dissolved oxygen meter which uses a polarographic system was used for the oxygen

Table 2.2

Composition of Groundwater Used in Soil Column and
Batch Equilibrium Sorption Tests

<u>Chemical Species</u>	<u>Concentration, mg/L</u>	
	<u>W 78</u>	<u>W 19</u>
Ca ⁺⁺	44	48
Mg ⁺⁺	14	18
SiO ₂	18	26
Fe (total)	<0.02	<0.02
Na ⁺	8.2	8.5
K ⁺	1.6	2.1
Cl ⁻	7.4	12
SO ₄ ⁼	22	24
HCO ₃ ⁻	207	206
O ₂	7.4 ^a	7.6 ^a
pH	8.1	8.0
Eh	0.75 ^v ^b	0.75 ^v ^b

^a Measured at 23⁰C. Air-saturated O₂ concentration at 23⁰C = 7.4 mg/L

^b Calculated value based on dissolved oxygen concentration.

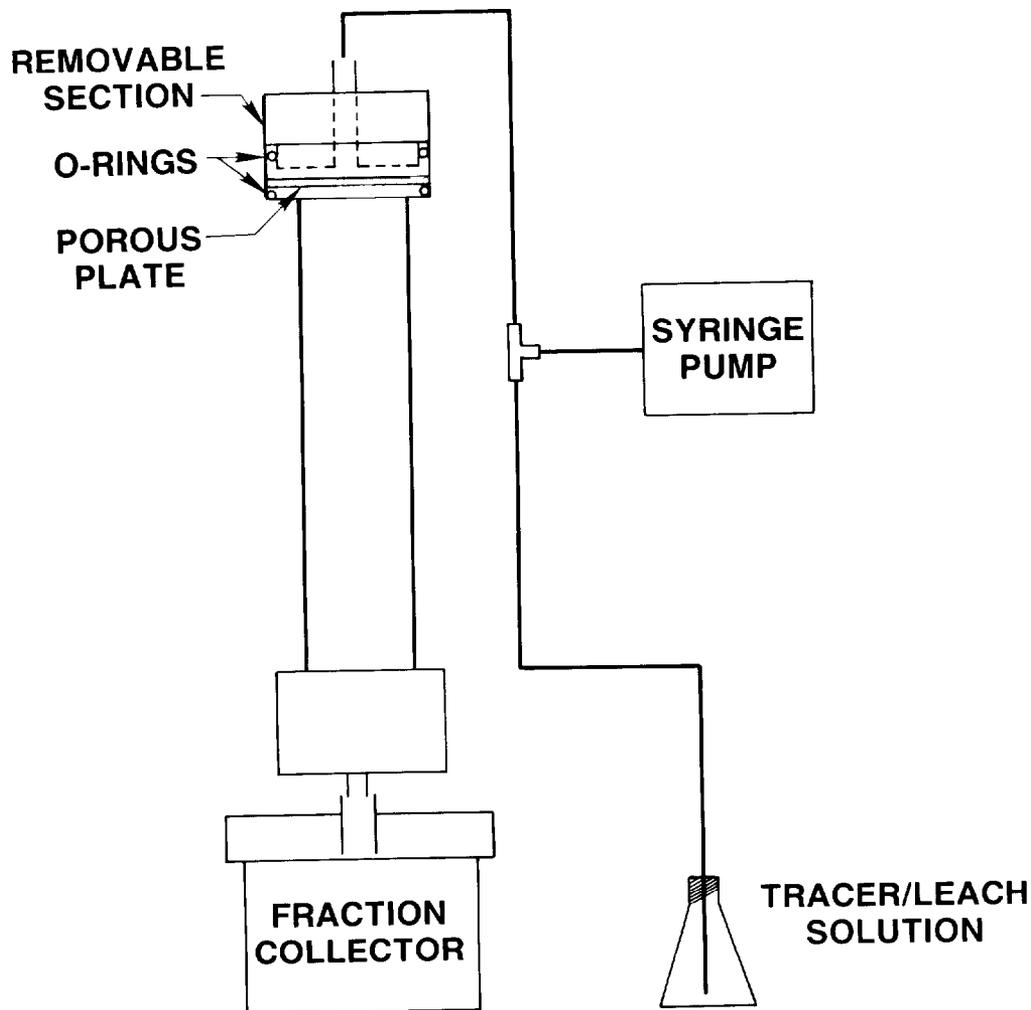
measurements. Redox potentials (Eh) were calculated from dissolved oxygen concentrations assuming that oxygen was the principal oxidative species in the groundwater.

III. SOIL COLUMN TESTS

1. SOIL COLUMN PREPARATION

The experimental apparatus used for the soil column studies is schematically illustrated in Figure 3-1. The equipment includes a 30-cm long x 5-cm i.d. Plexiglass column, a syringe pump and a fraction collector. The end assembly of the column consists of stationary and removable sections each containing an O-ring seal. The stationary section contains a porous stainless steel plate. The volume of the end assembly is minimized in order to reduce mixing. The syringe pump is a multi-channel, constant-volume pump which delivers an accurate volume over a set time interval. The Plexiglass column and syringe pump were purchased from Soil Measurement Systems, Las Cruces, New Mexico, 88001. The fraction collector is an Isco Retriever II (Isco, Inc., P.O. Box 5347, Lincoln, Nebraska, 68505).

Prior to packing the column, the materials were crushed and passed through a 2-mm sieve. Crushing of the alluvial and interbed sediments was minimized so as not to alter the particle size distribution. The materials were added to the column in small increments through a long-stemmed funnel. After the addition of each increment, the materials were vibrated on a Syntron vibration table (Model J-1, FMC Corporation, Homer City, PA 15748) at a setting of 10 for 2 minutes, then tamped with a 4.6-cm o.d. Teflon rod. The soil column was slowly saturated by pumping water upward at a flow rate of 0.1 mL/min until a constant weight was achieved and the soil was completely purged of air. The flow was then directed downward and the flow rate increased to 0.8 mL/min. The soil column was then purged with a downward flow and weighed several times until constant weight was reached. Total pore volume was assumed to be the volume of water in the soil column at saturation as measured by the difference between soil column weights before and after saturation.



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Figure 3-1. Schematic of Apparatus Used in the Soil Column Studies.

Corrections were made for the volume of the end assemblies and associated fittings. Table 3.1 lists the soil column characteristics. Estimations of sphericity and roundness¹⁰ indicated that the interbed soil particles were significantly more irregularly shaped than the alluvial particles. This characteristic as well as a lower particle density (see Table 2.1) accounted for the low packing bulk density and greater pore volume and porosity of the interbed soil column.

Table 3.1

Soil Column Characteristics

	Interbed		
	<u>Alluvium</u>	<u>Sediment</u>	<u>Basalt</u>
Bulk Density, g/cm ³	1.57	1.26	2.05
Total Pore Volume, cm ³	254	320	197
Porosity (void fraction)	0.43	0.53	0.33
Time Required for Saturation, hr	312	427	216

2. SOLUTE TRANSPORT THROUGH A SOIL COLUMN: THEORY AND DATA ANALYSIS

Solute transport through a soil column can be described by the one-dimensional, convective-dispersive equation:¹¹⁻¹⁴

$$R \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} - v \frac{\partial C}{\partial x} \quad (1)$$

where, R = retardation factor, water velocity/solute velocity
 C = aqueous solute concentration
 t = time, sec
 D = dispersion coefficient, cm²/sec
 v = average linear velocity (pore-water velocity)
 x = distance traveled through soil column

The term for radioactive decay of the solute was not included in the above equation because the Tc-95m and Se-75 tracers used for experimentation have long half-lives (60 and 120 days, respectively) relative to the time the solute passed through the column (12-24 hr).

Determination of retardation factors and dispersion coefficients from observed concentration distributions in a soil column are based on analytical solutions to the solute transport equation. The analytical solution to this equation expressed in terms of dimensionless constants and which can be applied to soil column studies for a pulse source of solute is:

$$\begin{aligned}
C(L,T)/C_0 &= 1/2 \operatorname{ERFC}[(P/4RT)^{1/2}(R-T)] & (2) \\
&+ 1/2 \operatorname{EXP}[P] \cdot \operatorname{ERFC}[(P/4RT)^{1/2}(R+T)] \\
&- 1/2 \operatorname{ERFC}[(P/4R(T-T_0))^{1/2}(R-(T-T_0))] \\
&- 1/2 \operatorname{EXP}[P] \cdot \operatorname{ERFC}[(P/4R(T-T_0))^{1/2}(R+(T-T_0))]
\end{aligned}$$

where: $C(L,T)/C_0$ = the normalized effluent concentration ranging from 0 to 1

L = length of soil column, cm

T = vt/L = time expressed as the number of displaced pore volumes

= $\frac{\text{volume of water collected at time } t}{\text{total pore volume}}$

T_0 = vt_0/L = pulse time expressed as the number of pore volumes displaced

t_0 = pulse time in minutes

P = vL/D = the Peclet No. which characterizes the height to width of the effluent curve.

ERFC = complimentary error function

The above analytical solution is for a semi-infinite column length of zero to infinity and flux-averaged concentrations. Equation (2) was fitted to the column effluent data (C/C_0 and T) by optimizing R , P and T_0 using a least-squares fitting routine. Applicability of equation (2) to the effluent data was made under the following assumptions:

1. The solute exists only as one species.
2. The soil column is homogeneous with uniform packing.
3. Water velocity is constant.
4. Linear equilibrium sorption occurs in the soil column.

The effluent curve is Gaussian-shaped and the effects of the variables R , P and T_0 are to:

1. shift the curve along the horizontal (T) axis as R increases,
2. increase curve height to band width as P increases, and
3. increase the area under the curve as T_0 increases.

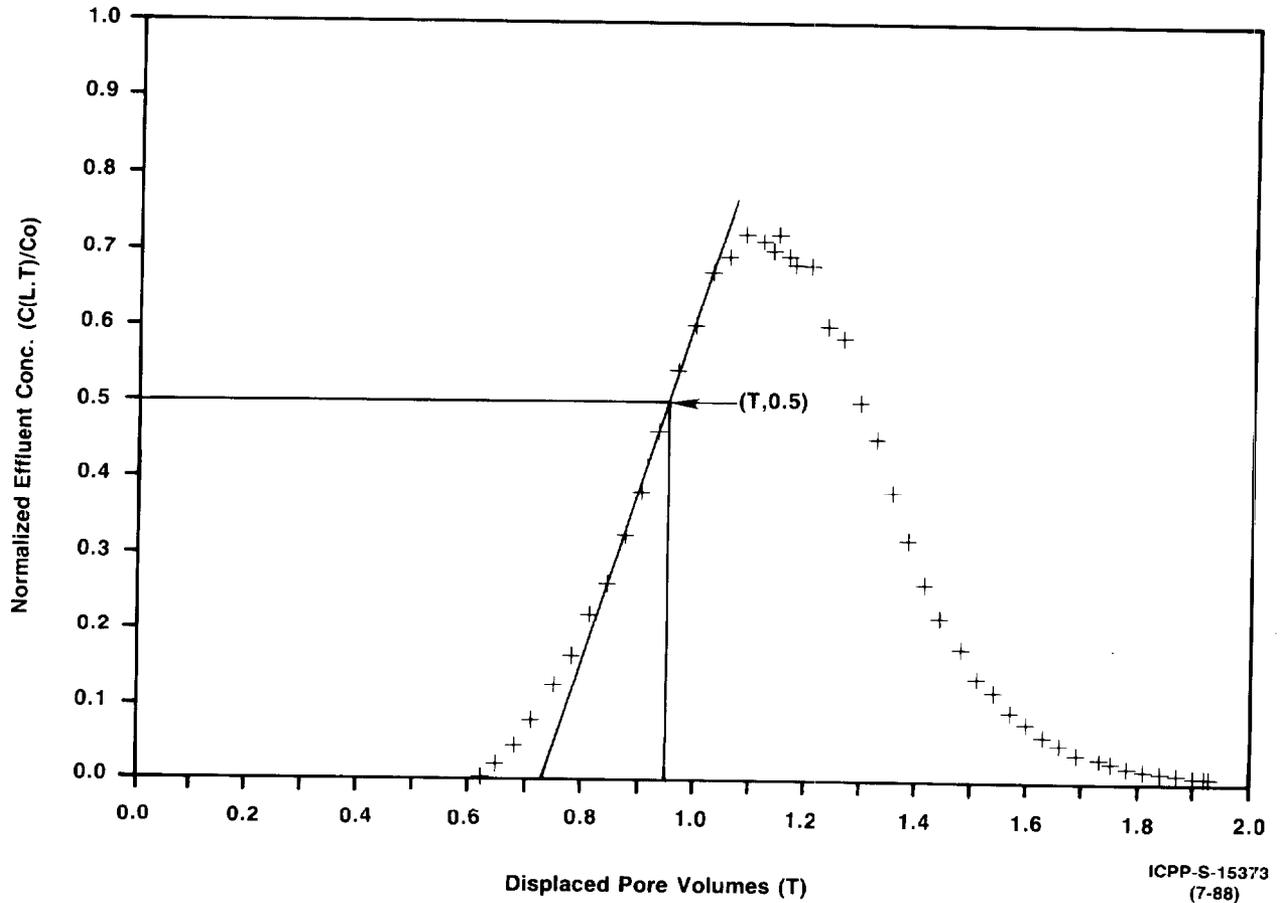


Figure 3-2. Method of Estimating R & P from Measured Data Points.

Curve fitting results have indicated that the second and fourth terms of equation (2) could be omitted without significant effects on R, P and T_0 . Van Genuchten and Wierenga¹⁰ also found this to be true. The variables R and P can be estimated from a hand plot of the data from the left side of the Gaussian-shaped breakthrough curve.¹⁰ The method is graphically illustrated in Figure 3-2. The first term of equation (2) is as follows:

$$C(L,T)/C_0 = 1/2 \operatorname{ERFC}[(P/4RT)^{1/2}(R-T)]$$

This term approximates the S-shaped (left side) of the Gaussian-shaped curve. When $T = R$, $R-T = 0$, $\text{ERFC}[0]=1$ and $C(L,T/C_0) = 0.5$. Therefore, by plotting $C(L,T)/C_0$ vs the number of displaced pore volumes of water (T), an estimate of R can be obtained by determining the value of T at $C(L,T)/C_0 = 0.5$ on the curve. The slope of the line passing through the point $(T,0.5)$ is measured and an approximation for P is obtained from equation (3).

$$P = 4 \pi R^2 (\text{slope})^2 \quad (3)$$

Referring to Figure 2, $R = 0.95$ and the slope = 2.38. Therefore, $P = 64$.

3. EXPERIMENTAL PROCEDURE

The soil column experiments were conducted using a solute displacement method in which a pulse of tracer solution was added to the soil column followed by a displacing solution (groundwater). The flow rate chosen for the experiments, 0.80 mL/min, was based on measured water infiltration rates in the vadose zone under saturated conditions. Pulse times varied from 2 to 4 hr and the time required for complete tracer displacement from the soil column varied from 12 to 24 hr. All tests were conducted at ambient temperature. The tracers used were $\text{Na}^{95\text{m}}\text{TcO}_4$, $\text{Na}_2^{75}\text{SeO}_4$, $\text{Na}_2^{75}\text{SeO}_3$, and tritiated water (HTO). The HTO was used in order to provide a reference to water transport properties. Only one tracer was used for each displacement run. Technetium tracer solutions were carrier-free and ranged from 1.8×10^{-4} to $9.9 \times 10^{-4} \mu\text{Ci/L}$ (8×10^{-17} to $4.5 \times 10^{-16} \text{ M}$). The carrier concentration of the selenium tracer solutions was $9.6 \times 10^{-6} \text{ M}$. The column effluent was collected in 4-ml fractions. Technetium and selenium concentrations were measured using standard gamma-counting techniques and HTO was measured by scintillation counting. Tracer concentrations were measured in counts/minute/mL.

4. RESULTS AND DISCUSSION

Least-squares fitted plots of equation (2) to column effluent data for TcO_4^- , $\text{SeO}_4^{=}$, $\text{SeO}_3^{=}$ and HTO are shown in Figures 3-3, 3-4 and 3-5. The symbols shown in the plots represent measured data points. The breakthrough curves indicate that optimization of R, P and T_0 resulted in good fits of equation (2) to the measured data points. Equation (2), therefore, adequately describes convective-dispersive, solute-transport in the soil columns studied. The poorest fit generally occurs in the tailed section of the breakthrough curve. Transport equations which account for tailing in effluent curves by considering mass transfer of solute from mobile to immobile water in the soil have been developed.¹⁵ The transport properties determined for pertechnetate (TcO_4^-), selenate ($\text{SeO}_4^{=}$), selenite ($\text{SeO}_3^{=}$) and tritium (HTO) in alluvium, interbed sediment and basalt are listed in Table 3.2. The standard deviations of the least-squares fitted plots of equation (2) to the measured data points are also listed. The data indicate no retardation of TcO_4^- or $\text{SeO}_4^{=}$, relative to water, and a significant retardation of $\text{SeO}_3^{=}$ in the alluvium and interbed sediment. A slight retardation of $\text{SeO}_3^{=}$ in basalt was also indicated. Retardation factors for TcO_4^- and $\text{SeO}_4^{=}$ were observed to be less than for HTO in these materials. This effect is generally thought to be attributed to anion exclusion in which anionic solutes are repulsed by the negatively-charged soil particles and concentrate near the center of a pore space where fluid velocities are greater than in the total pore space. Both sediments exhibited an affinity for $\text{SeO}_3^{=}$ as evidenced by significant sorption on the soil column under the experimental conditions of the study. Selenite has been observed to bind strongly to hydrous ferric oxides such as goethite ($\alpha\text{-FeOOH}$) and $\gamma\text{-Fe}_2\text{O}_3$ as well as various clays.^{16,17} It is possible that the amorphous iron oxides present in the soils tested may account for the sorption of $\text{SeO}_3^{=}$. Estimates of retardation factors for $\text{SeO}_3^{=}$ have been determined with the batch equilibrium sorption method (see Section IV).

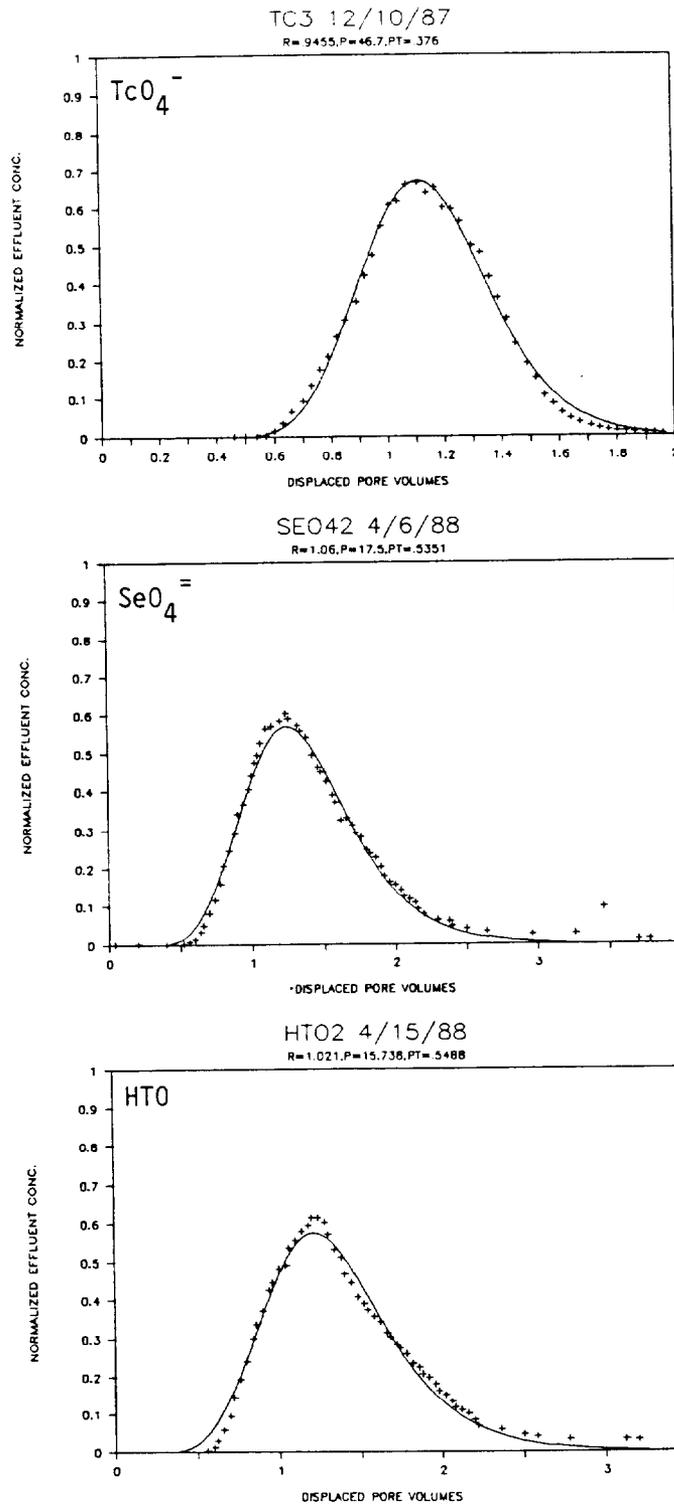


Figure 3-3. Non-Linear Least-Squares Fitted Plots of Equation (2) to Column Effluent Data for Alluvium.

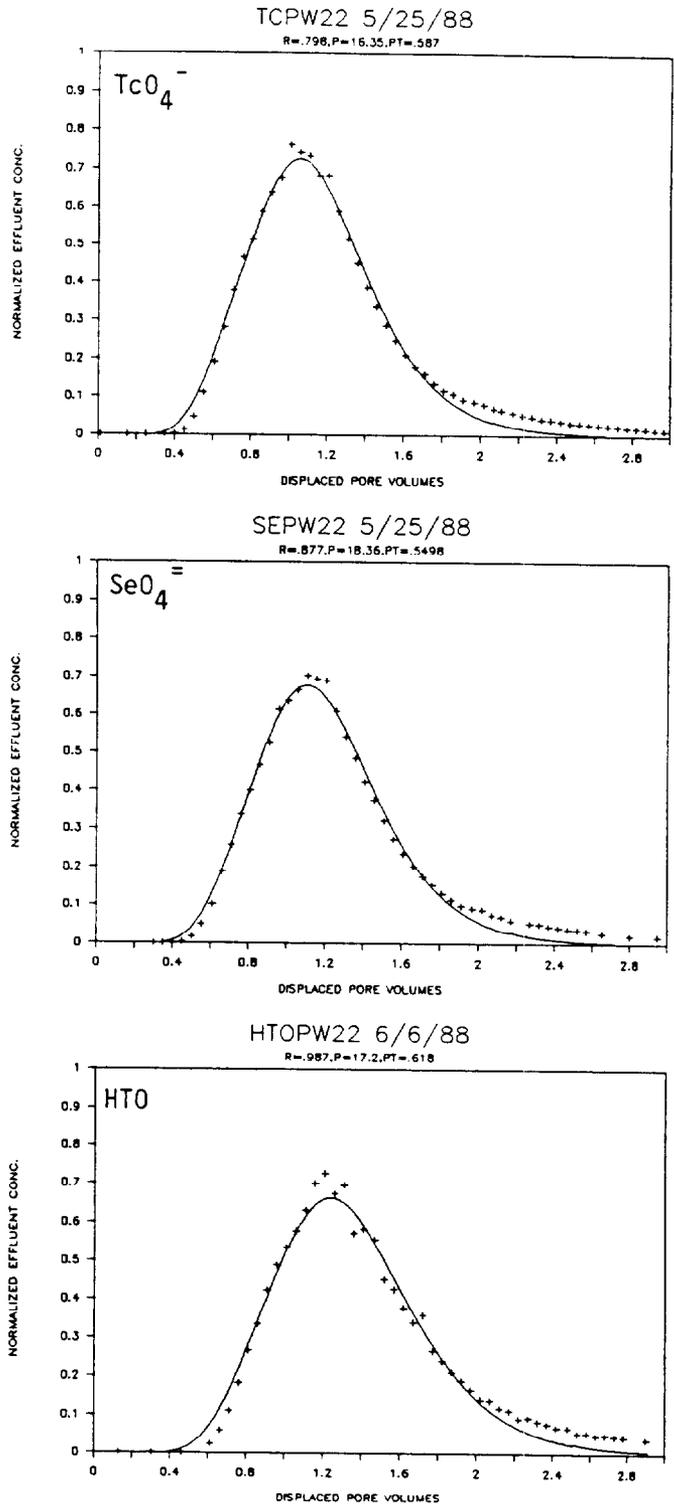


Figure 3-4. Non-Linear Least-Squares Fitted Plots of Equation (2) to Column Effluent Data for Interbed Sediment.

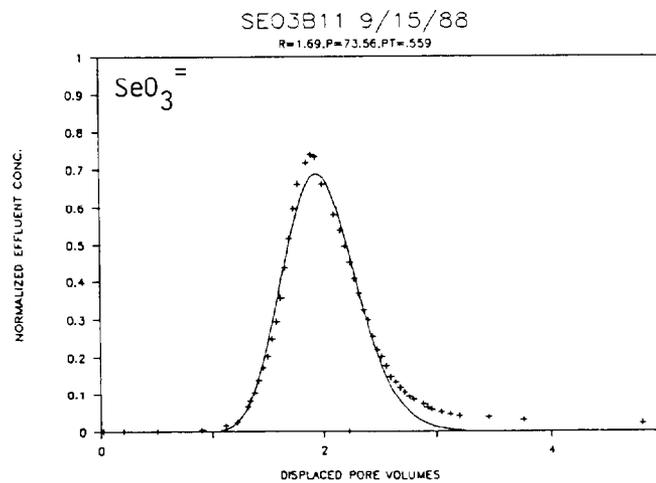
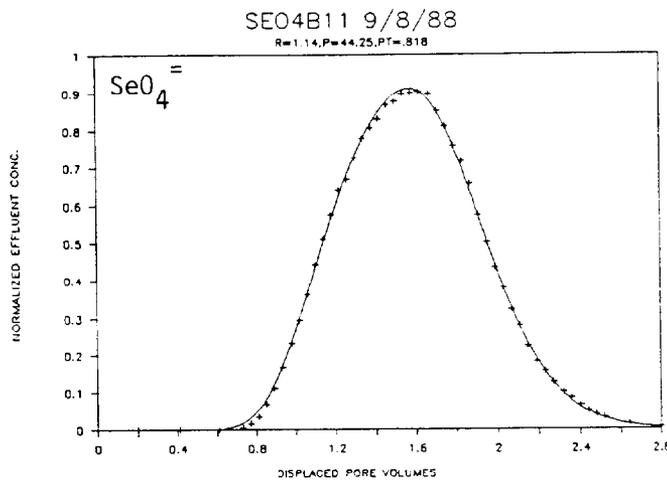
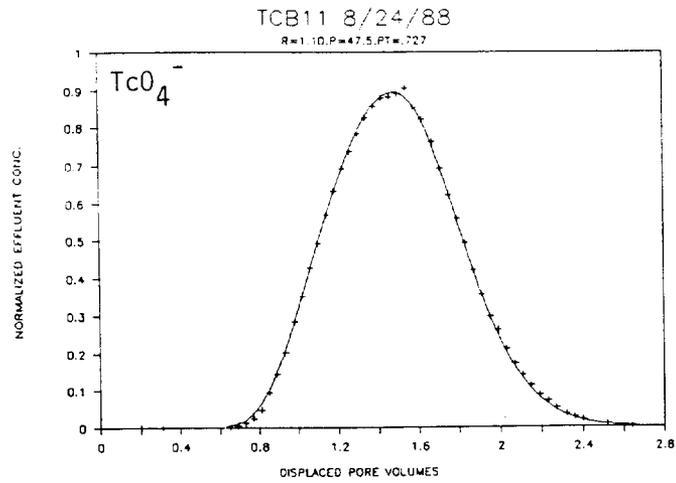


Figure 3-5. Non-Linear Least-Squares Fitted Plots of Equation (2) to Column Effluent Data for Basalt

Table 3.2

Measured Transport Properties of Pertechnetate, Selenate,
Selenite, and Tritium (HTO) in Alluvium, Interbed Sediment, and Basalt

<u>Alluvium</u>						
<u>Run #</u>	<u>Species</u>	<u>Retardation Factor, R</u>	<u>Peclet No. P</u>	<u>Dispersion Coefficient, D (cm²/day)</u>	<u>Pulse Time, T₀</u>	<u>Standard Deviation of Fit, %</u>
TC2	TcO ₄ ⁻	0.94	58	68	0.372	2.1
TC3	TcO ₄ ⁻	0.95	47	83	0.376	1.1
TC4	TcO ₄ ⁻	0.94	55	70	0.220	1.9
SE042	SeO ₄ ⁼	1.06	18	228	0.535	2.1
SE043	SeO ₄ ⁼	1.02	15	267	0.518	2.7
HTO2	HTO	1.02	16	247	0.549	2.6
SE031	SeO ₃ ⁼	Significant Retardation ^a			0.385	
SE032	SeO ₃ ⁼	Significant Retardation			0.210	
<u>Basalt</u>						
TCB11	TcO ₄ ⁻	1.10	48	110	0.727	1.0
SE04B11	SeO ₄ ⁼	1.14	44	132	0.818	1.0
SE03B11	SeO ₃ ⁼	1.70	74	79	0.559	3.1
<u>Interbed Sediment</u>						
TCPW21	TcO ₄ ⁻	0.78	21	151	0.261	2.2
TCPW22	TcO ₄ ⁻	0.80	16	201	0.587	2.4
SePW21	SeO ₄ ⁼	0.88	18	188	0.549	2.1
SePW22	SeO ₄ ⁼	0.88	18	179	0.550	2.3
HTOPW22	HTO	0.99	17	192	0.500	3.3
Se03PW21	SeO ₃ ⁼	Significant Retardation ^a			0.171	

^a Due to retention of SeO₃⁼, no column effluent data were obtained.

Peclet numbers for runs TC2, TC3 and TC4 were considerably larger than for all succeeding runs. This may have been due to a change in soil column characteristics brought about by settling of the soil particles. As a result of the larger Peclet numbers for these runs, calculated dispersion coefficients were much lower than for all other runs. The dispersion coefficient is a function of the average linear velocity (pore-water velocity) which is inversely dependent on the porosity of the soil. Therefore, due to variations in the porosity, solute dispersion in undisturbed field soils may vary considerably from that measured in displacement experiments with repacked soils.

IV. BATCH EQUILIBRIUM SORPTION TESTS

1. EQUILIBRIUM SOLUTE SORPTION ON POROUS MEDIA

The equilibrium sorption of solutes on porous media can be described by the Freundlich isotherm equation:

$$S_m = k C_e^n \quad (4)$$

where,

S_m = moles of solute sorbed/g of soil

C_e = equilibrium solute concentration, moles/Liter

k and n = constants

As n approaches 1, solute sorption approaches linearity and k approaches the value of the distribution coefficient (Kd) measured by batch sorption experiments:

$$Kd = \frac{S_m}{C_e} \quad (5)$$

Equations (4) and (5) can be combined to give an expression which describes Kd as a function of the equilibrium solute concentration:

$$Kd = k C_e^{n-1} \quad (6)$$

As n approaches 1, Kd becomes less dependent on C_e and approaches k.

The distribution coefficient can be related to the relative velocity of a solute in porous media by the following expression:

$$R = 1 + \frac{Kd \rho}{\theta} \quad (7)$$

where,

- R = retardation factor, solvent velocity/solute velocity
- Kd = distribution coefficient, mL/g
- ρ = bulk density of soil, g/cm³
- θ = fraction of total column volume occupied by water = porosity at saturation

Equation (7) is an empirical, mass balance-derived expression from chromatographic theory that has been derived by several authors.^{18,19,20} It is applicable only when solute sorption is linear, that is when Kd is constant as the solute moves through the soil. In the case of non-linear sorption where Kd is dependent on the equilibrium solute concentration and varies during solute migration, equation (8) can be used to estimate a retardation factor range based on a range of equilibrium solute concentrations.¹⁴ Equation (8) can be used to compare retardation factors determined by soil column methods to those obtained from batch equilibrium sorption techniques.²⁰

$$R = 1 + \frac{\rho}{\theta} knC_e^{n-1} \quad (8)$$

2. EXPERIMENTAL PROCEDURE

Sorption data for cadmium, mercury, selenium (as SeO₃⁼) and strontium on alluvium, interbed sediment and basalt were obtained using the batch equilibrium sorption method. This method involved adding 1 g of material into each of a series of 50 mL centrifuge tubes and then adding measured volumes of tracer stock solution, non-radioactive metal stock solution and groundwater such that the series contained a range of initial metal concentrations. Each tube in the series was prepared in triplicate. The final volume in each tube was 20 mL. Stock solutions were adjusted to pH 8 when necessary. Blanks, which consisted of tubes containing test solutions without soil were prepared to account for sorption on the centrifuge tube. The tubes were placed in a constant temperature shaker

bath at 30°C for 6 days to allow for equilibration. After equilibration, all tubes were centrifuged and aliquots of the solutions were gamma-counted to measure the remaining activity. The amount of metal sorbed was determined as follows:

$$S_m = \frac{(A_{rb} - A_{rs}) V_t R_a}{G}$$

where,

- S_m = moles of metal sorbed/gram of material
- A_{rb} = activity remaining in solution blank, cpm/mL
- A_{rs} = activity remaining in sample solution, cpm/mL
- V_t = total volume of solution, mL
- R_a = moles of metal in solution/activity in solution at equilibrium, moles/cpm
- G = grams of material
- cpm = counts/minute

The tracer stock solution was counted with the samples to account for radioactive decay in determining the ratio, R_a .

The equilibrium metal concentration was determined as follows:

$$C_e = A_{rs} R_a 10^3$$

where,

- C_e = equilibrium metal concentration, moles/Liter

The tracers used were Cd-109, Hg-203, Se-75 and Sr-85. Equilibration times were determined by preparing a set of six tubes each having 1 g of soil and the same initial metal concentration. Aliquots from each tube in succession were counted each day until the percentage of sorbed activity remained the same.

3. DATA ANALYSIS

Sorption isotherms for the metals studied were obtained by fitting equation (4) to the measured values for the moles of metal sorbed (S_m) and the equilibrium metal concentration (C_e). This was done by first taking the natural logarithm of both sides of equation (4):

$$\ln S_m = n \ln C_e + \ln k \quad (9)$$

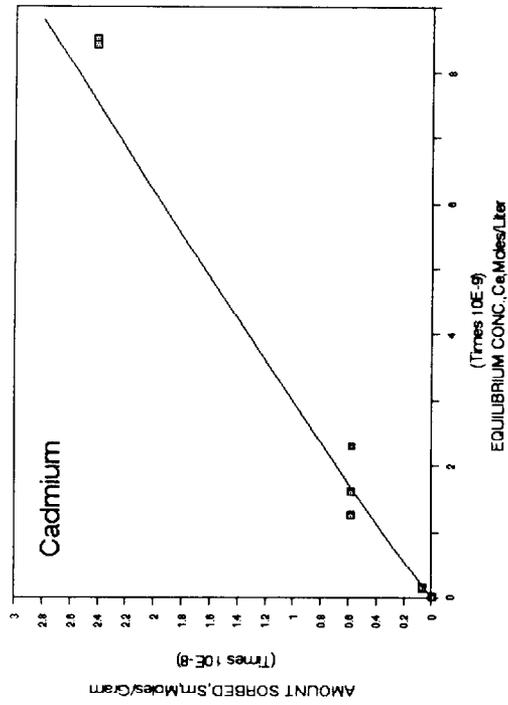
Using measured values for S_m and C_e , a linear regression was performed on equation (9) to obtain values for k and n . The isotherm was then constructed by using equation (4) to calculate values of S_m for a range of C_e values. Retardation factors were calculated by using equation (7).

4. RESULTS AND DISCUSSION

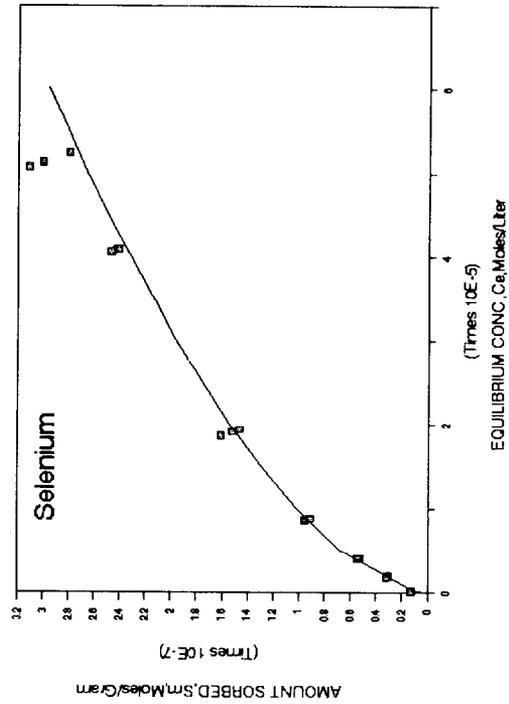
Isotherms for the sorption of cadmium, mercury, selenium and strontium on alluvium and interbed sediment are shown in Figures 4-1 and 4-2. The symbols shown in the plots are the measured data points in groups of three representing replicate determinations. Due to scale constraints and the close proximity of the measured data points at the lower end of the graphs, these data points tended to be superimposed on one another. The isotherms indicate that sorption of cadmium and strontium was approximately linear while sorption of mercury and selenium was non-linear within the equilibrium concentration ranges studied. Good fits of equation (4) to the measured data points were obtained indicating that the Freundlich isotherm equation adequately describes sorption of the metals studied under the test conditions. Isotherms for the sorption of cadmium and mercury on basalt are not shown due to very poor fits of equation (4) to the measured data points. Due to the very low sorption of selenium and strontium on basalt, no attempt was made to obtain isotherms for these metals.

Table 4.1 summarizes the data for the sorption of the metals studied on alluvium, interbed sediment and basalt. Cadmium was strongly sorbed on all the geologic materials as evidenced by very large K_d values. The large K_d

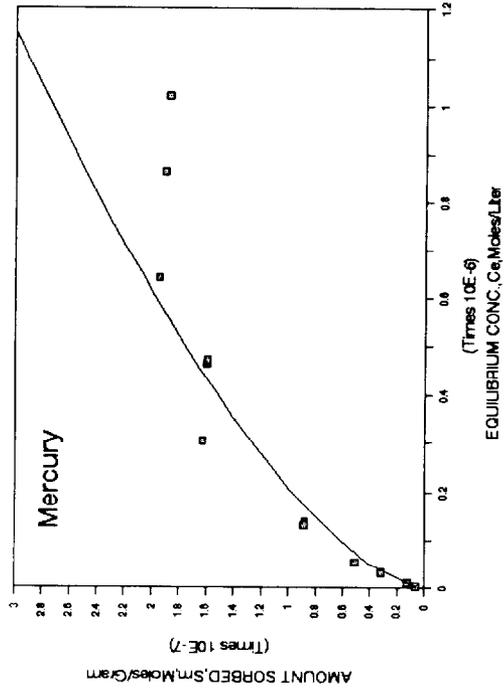
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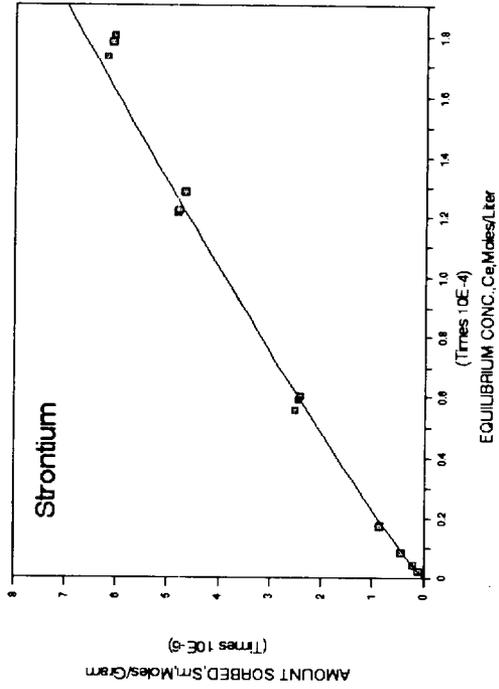


Figure 4-1. Sorption Isotherms for Cadmium, Mercury, Selenium, and Strontium on Alluvium.

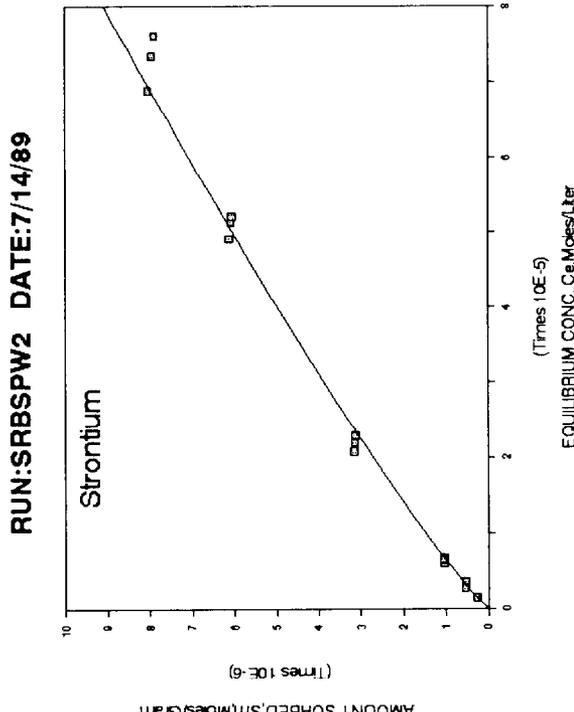
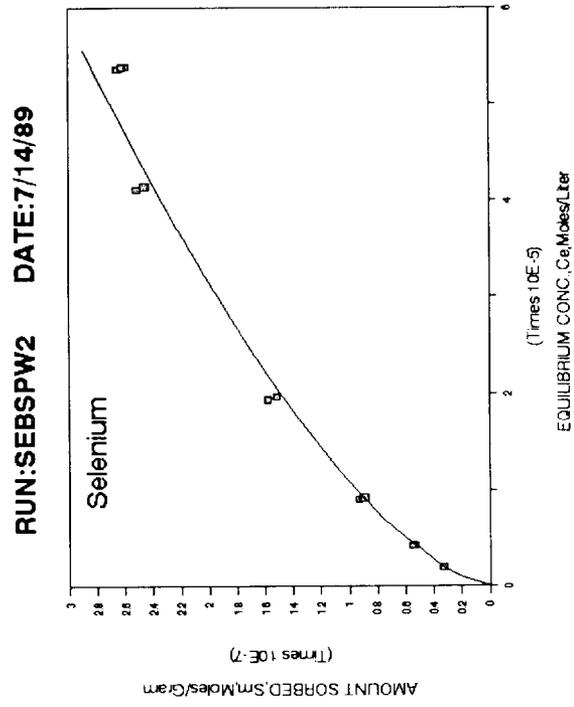
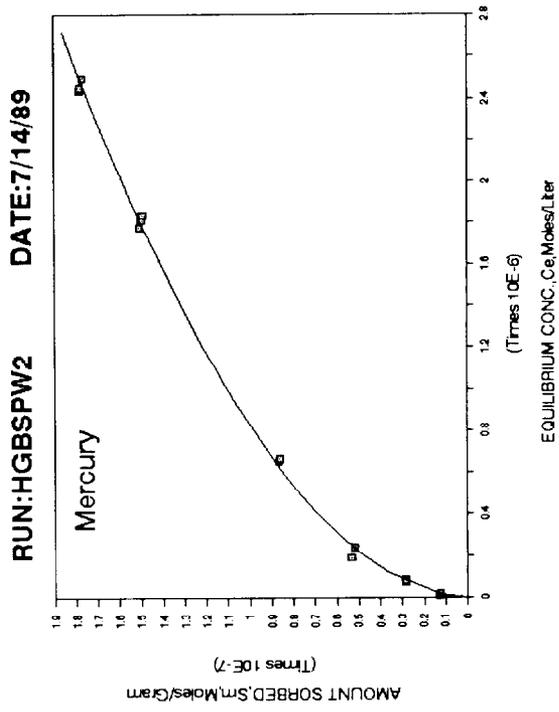
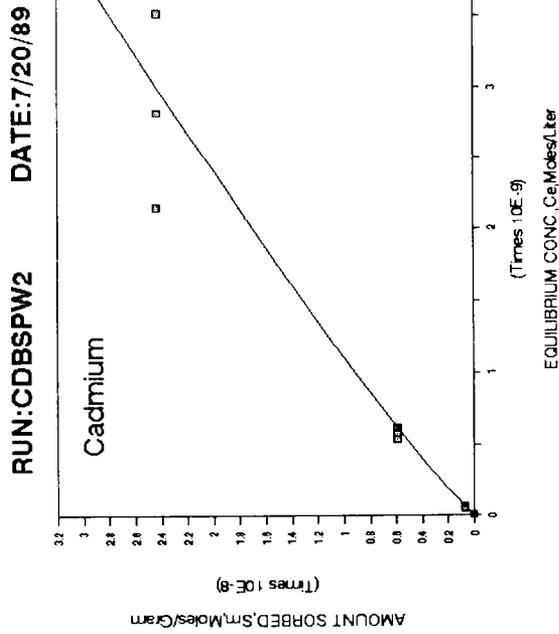


Figure 4-2. Sorption Isotherms for Cadmium, Mercury, Selenium, and Strontium on Interbed Sediment

Table 4.1

Summary of Data for Equilibrium Sorption of Metals on Geologic Materials

Geologic Material	Metal	Initial Concentration Range, M	Measured Kd Range (mL/g)	Freundlich Constants		Retardation Factor Range ^a
				k (mL/g)	n	
Interbedded Sediment	Cd	3.7x10 ⁻⁹ - 1.5x10 ⁻⁶	10,115-8622	1000	0.89	24,048-20,499
	Hg	6.5x10 ⁻⁷ - 1.0x10 ⁻⁵	673-72	0.148	0.52	1601-172
	Se	3.5x10 ⁻⁶ - 6.6x10 ⁻⁵	17-4.9	0.165	0.65	41.4-12.7
	Sr	1.5x10 ⁻⁵ - 4.8x10 ⁻⁴	186-110	32.7	0.87	443-263
Alluvium	Cd	3.7x10 ⁻⁹ - 1.5x10 ⁻⁶	4891-2864	1177	0.95	17,745-10,391
	Hg	3.3x10 ⁻⁷ - 1.0x10 ⁻⁵	1912-236	1.89	0.64	6938-857
	Se	8.6x10 ⁻⁷ - 6.6x10 ⁻⁵	63-5.8	0.096	0.60	230-22
	Sr	7.7x10 ⁻⁶ - 4.8x10 ⁻⁴	52-35	17	0.91	190-128
Basalt	Cd	3.7x10 ⁻⁹ - 1.5x10 ⁻⁶	2319-785	c	c	14,407-4878
	Hg	6.9x10 ⁻⁷ - 1.0x10 ⁻⁵	87-9.2	c	c	542-58
	Se ^b	4.3x10 ⁻⁷	3.4	n.d.	n.d.	22
	Sr ^b	6.6x10 ⁻⁵	0.29	n.d.	n.d.	2.8
		7.6x10 ⁻⁶	2.7	n.d.	n.d.	17.8
		4.8x10 ⁻⁴	1.1	n.d.	n.d.	7.8

^a Retardation factor (R) = water velocity/solute velocity. R values calculated with equation (7) using measured Kd values.

^b Due to very low sorption, only high and low initial metal concentrations were used. No isotherms were plotted.

^c k and n not listed due to poor fits of equation (1) to data. n.d. Not determined.

values obtained may have been partly due to the precipitation of CdCO_3 ($K_{sp} = 1.8 \times 10^{-14}$). Although blanks consisting of metal solutions but no soil were run to account for species precipitation, it is possible that the presence of the soil induced precipitation of CdCO_3 . It is also possible that the extremely fine precipitate adhered to the soil but did not settle during centrifugation of the blanks. Mercury sorption was large to moderate on the interbed sediment, large on the alluvium and moderate on basalt. Selenium sorption was low on the interbed sediment, very low on basalt and moderate to low on the alluvium. Strontium sorption was large on the interbed sediment, moderate on alluvium and very low on basalt. Retardation factors for alluvium and interbed sediment ranged from very large to large for all species except selenium. Since basalt is largely monolithic, sorption data for crushed basalt may not be applicable to field conditions except where fine material exists. However, considerable retention of cadmium and mercury may occur given sufficient contact time of the percolating solution with the basalt. The non-linear sorption characteristics of mercury and selenium are indicated in the table by the considerable dependence of their distribution coefficients (K_d) on initial metal concentrations and by values of n much less than 1. The dependence of K_d on the initial metal concentration will have to be taken into account when developing transport models. It may be possible to incorporate equation (8), which relates the retardation factor to the equilibrium solute concentration into the TRACR3D modeling code.²²

Tables 4.2 and 4.3 list initial metal concentrations and distribution coefficients for the sorption of metals on alluvium and interbed sediment. The data indicate that distribution coefficients increased with decreasing initial metal concentrations. This effect was much greater for mercury and selenium than for cadmium and strontium, as was indicated by the non-linear sorption isotherms. Tests with cadmium solutions greater than $1 \times 10^{-6} \text{ M}$ indicated 100% sorption of cadmium on the centrifuge tube. This was most likely due to precipitation of CdCO_3 indicating that the movement of cadmium through the soil will be limited by the solubility of CdCO_3 as well as by cadmium sorption. Similar data for strontium indicated that its movement will be limited by the solubility of SrCO_3 which precipitated at

Table 4.2

Distribution Coefficients and Initial Metal Concentrations
for Sorption of Metals on Interbed Sediment

Sample	Initial Concentration, M	Distribution Coefficients ^a		% Relative Standard Deviation ^c
		Kd, Calc. ^b (mL/g)	Kd, Meas. (mL/g)	
Cd6	1.51×10^{-6}	8,737	8,978	± 25
Cd7	3.89×10^{-7}	10,375	10,251	± 7.3
Cd8	3.89×10^{-8}	13,373	12,895	± 12
Hg7	1.04×10^{-5}	72.9	72.4	± 1.6
Hg6	8.46×10^{-6}	84.5	83.1	± 2.3
Hg5	4.56×10^{-6}	138	133	± 1.6
Hg4	2.61×10^{-6}	223	218	± 0.23
Hg3	1.63×10^{-6}	386	374	± 5.5
Hg2	6.51×10^{-7}	755	673	± 4.7
Se7	6.64×10^{-5}	5.15	4.88	± 1.2
Se6	5.29×10^{-5}	5.65	5.99	± 1.8
Se5	2.68×10^{-5}	7.35	8.02	± 3.4
Se4	1.34×10^{-5}	9.56	9.86	± 3.1
Se3	6.84×10^{-6}	12.5	12.9	± 2.6
Se2	3.53×10^{-6}	16.4	16.5	± 1.0
Sr7	4.83×10^{-4}	113	110	± 6.0
Sr6	3.63×10^{-4}	118	120	± 3.7
Sr5	1.81×10^{-4}	132	144	± 5.3
Sr4	6.04×10^{-5}	155	166	± 5.7
Sr3	3.03×10^{-5}	170	173	± 17
Sr2	1.52×10^{-5}	188	186	± 5.9

^a Average of three replicate determinations.

^b Kd calculated with equation (6).

^c % Relative Standard Deviation = (standard deviation/mean) x 100.

Table 4.3

Distribution Coefficients and Initial Metal
Concentrations for Sorption of Metals on Alluvium

Sample	Initial Concentration, M	Distribution Coefficients ^a		% Relative Standard Deviation ^c
		Kd, Calc. ^b (mL/g)	Kd, Meas. (mL/g)	
Cd6	1.51×10^{-6}	2981	2864	$\pm 0.77^d$
Cd7	3.89×10^{-7}	3233	3636	± 29
Cd8	3.89×10^{-8}	3645	4891	± 5.9
Cd9	3.68×10^{-9}	4028	3489	$\pm 12^d$
Hg7	1.04×10^{-5}	293	236	± 26
Hg6	8.45×10^{-6}	380	407	± 28
Hg5	4.55×10^{-6}	564	662	± 3.0
Hg4	2.60×10^{-6}	790	972	± 3.2
Hg3	1.63×10^{-6}	952	1023	± 4.3
Hg2	6.5×10^{-7}	1417	1239	± 2.3
Hg1	3.25×10^{-7}	2121	1912	± 8.6
Se7	6.65×10^{-5}	4.98	5.77	± 7.0
Se6	5.30×10^{-5}	5.31	5.98	± 1.7
Se5	2.68×10^{-5}	7.41	8.02	± 6.7
Se4	1.35×10^{-5}	10.1	10.7	± 3.6
Se3	6.85×10^{-6}	13.6	12.8	± 2.8
Se2	3.54×10^{-6}	18.4	16.1	± 3.4
Se1	8.60×10^{-7}	45.4	63.2	$\pm 2.6^d$
Sr7	4.84×10^{-4}	37.0	34.7	± 3.2
Sr6	3.63×10^{-4}	38.2	38.5	± 4.5
Sr5	1.82×10^{-4}	40.9	42.3	± 6.1
Sr4	6.05×10^{-5}	45.6	49.6	± 2.8
Sr3	3.04×10^{-5}	48.5	49.9	± 1.9
Sr2	1.53×10^{-5}	51.8	52.0	e
Sr1	7.65×10^{-6}	55.1	52.1	± 4.7

^a Average of three replicate determinations.

^b Kd calculated with equation (6).

^c % Relative Standard Deviation = (standard deviation/mean) x 100.

^d Two determinations.

^e One determination.

concentrations greater than about 1×10^{-3} M. Mercury is expected to precipitate as HgO at concentrations greater than 1×10^{-4} M.⁶ Selenite is not expected to have any solubility limitations in the groundwater.

Tables 4.2 and 4.3 also list the distribution coefficients calculated with equation (6) which, when compared with the measured distribution coefficients give an indication of the goodness of fit of equation (4) to the measured data points. The data indicate that good agreement between the two distribution coefficients was obtained. The precision of the three replicate measurements of the measured distribution coefficients is indicated by the percent relative standard deviation (RSD). With very few exceptions, precision was acceptable and in the range of 1 to 7% RSD. The wide variations of RSD observed for cadmium may have been due to variable amounts of cadmium carbonate precipitation.

The reported distribution coefficients and retardation factors are to be considered only as estimates of the sorption behavior of the species studied. These parameters may be influenced by 1) soil porosity, 2) compositional changes in the soil, 3) ionic strength of the groundwater, 4) soil/groundwater ratios, and 5) water content of the soil.

V. CONCLUSIONS

1. Technetium as the pertechnetate ion (TcO_4^-) and selenium as the selenate ion (SeO_4^{2-}) will not be retarded by the near-surface alluvium, interbed sediment or basalt under oxic, saturated conditions. A retardation factor of 1 can be assumed for transport models.
2. Due to very large retardation factors, cadmium should become fixed on alluvium and interbed sediment relative to groundwater. Strong retention on basalt may occur given sufficient contact time. Cadmium sorption is linear enabling the use of the TRACR3D modeling code without modification.
3. Mercury should be strongly sorbed on alluvium and interbed sediment. Migration rates could range from 1×10^{-4} to 6×10^{-3} times that of groundwater. Mercury sorption was non-linear (concentration dependent) suggesting that modeling codes which take into account non-linear sorption should be used to provide accurate transport models. At very low concentrations ($< 1 \times 10^{-7}$ M) mercury could become strongly retarded on basalt given sufficient contact time.
4. The migration rate of selenium (as SeO_3^{2-}) could range from 4×10^{-3} to 8×10^{-2} times that of water in alluvium and interbed sediment. Sorption behavior was non-linear indicating that non-linear sorption modeling codes may be necessary for transport modeling. Very little sorption will take place on basalt.
5. Strontium sorption on alluvium and interbed sediment was linear and migration rates could range from 2×10^{-3} to 8×10^{-3} times that of water. Sorption on basalt will be very low.
6. The Freundlich isotherm equation can be used to model the equilibrium sorption behavior of cadmium, mercury, selenium and strontium in order to determine distribution coefficients necessary for transport modeling.

7. The analytical solution to the one-dimensional, convective-dispersive solute-transport equation can be fitted to soil column effluent data for the purpose of measuring solute retardation factors and dispersion coefficients in laboratory soil columns for solutes exhibiting no significant retention.

VI. RECOMMENDATIONS

1. Soil column experiments should be conducted to measure retardation factors for mercury, strontium and selenite and the results compared to the batch equilibrium sorption data.
2. Batch equilibrium sorption tests should be conducted to measure distribution coefficients of mercury, selenium and strontium at groundwater temperatures of 10-16°C.
3. Soil column studies to determine retardation factors and dispersion coefficients of pertechnetate (TcO_4^-) and selenate (SeO_4^{2-}) under unsaturated conditions should be conducted since these conditions are more representative of the vadose zone.
4. Field measurements of water content, porosity and water migration rate should be obtained for the vadose zone under the ICPP to better model the transport of radionuclides and hazardous chemical species.

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