Monitoring and Physical Characterization of Unsaturated Zone Transport — Laboratory Analysis

**G. W. Gee
A. C. Campbell**

March 1980

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SUMMARY

Batch Kd screening tests using two Hanford sediments and a series of synthetic ground water solutions indicated that:

1. Anionic radionuclide mobility is dependent upon specie and concentration. Technetium, as TcO_4^- is not sorbed to any extent and will move as rapidly as water through Hanford sediments under shallow land burial conditions. Iodine, as I^- , will also move, if in high enough concentration (>5 ppb) but appears to be retarded at very low concentrations (<1 ppb). The exact mechanism for the sorption of iodine at these low concentrations has not been determined.
2. Neutral species such as tritium and complexed nuclides such as cobalt-60 (EDTA) are only slightly retarded while uncomplexed cobalt-60 is strongly bound to the sediments under the conditions studied.
3. Strontium sorption is controlled by ion exchange-like reactions and sorption is predictable from a knowledge of soil and solution characteristics. For conditions typical of burial grounds at Hanford, strontium would be transported a meter or less before decaying to undetectable levels.
4. Cesium is strongly bound to the Hanford sediments under typical conditions and appears to be sorbed independent of salt concentration for the synthetic ground waters tested. Movement of cesium will be insignificant at Hanford burial sites under normal conditions.

Unsaturated column studies on Hanford sediments indicated that:

1. The sorption of relatively mobile nuclides such as tritium, cobalt-EDTA, and technetium could be measured with greater precision using the unsaturated column tests than with batch methods. Although general agreement was obtained between the two methods, the adsorption coefficient (Kd) values for tritium, cobalt-EDTA, technetium and iodine were less variable and better defined with the unsaturated column tests than with batch tests. Kd values for strontium from unsaturated column tests agreed well with batch test determinations.

2. Little or no difference in sorption was observed when the flow rates were changes by more than an order of magnitude (2 to 50 cm/day).
3. Changes in saturation percentage of the soil, from 56 to 31%, also had only a minor effect on nuclide sorption.
4. For layered sediments, the effective sorption of a layered sequence is controlled by the sorption characteristics of the most sorbing layer.

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INTRODUCTION

The major pathway for transport of radionuclides from arid zone burial grounds is through unsaturated sediments. Although considerable effort has been expended over the past few years to quantify the mobility of nuclear wastes and determine factors that influence radionuclide mobility (Ames et al. 1976, Ahlstrom et al. 1977, Serne et al. 1977, Wolfsberg 1978, Relyea et al. 1979, and Serne et al. 1978), little work has been done to investigate the transport of radionuclides under conditions of partial saturation, the most common situation found at arid region burial sites.

Sorption of a radionuclide by geologic material can be quantified by measuring the radionuclide adsorption coefficient or K_d . The K_d is defined as the ratio of the amount of radionuclide sorbed on the solid surfaces of the test material to the amount of radionuclide remaining in solution measured at equilibrium or steady state conditions:

$$K_d = \frac{\text{Amount of Nuclide Sorbed}}{\text{Amount of Nuclide in Solution}} \quad (1)$$

A completely nonsorbing radionuclide has a K_d of 0 while a completely sorbed radionuclide would have a K_d of infinity.

The K_d for a particular radionuclide is dependent upon a number of factors. Factors of major importance include: the concentration and oxidation state of the radionuclide; the chemistry of the contact solution, including ionic strength and composition, and solution-sediment pH-Eh relationships; the properties of the geologic material including ion exchange capacity, organic matter content, mineralogy, and particle size distribution.

Tests used for K_d determinations include batch and column methods. The batch K_d method is a static test and normally uses a large solution-to-solid ratio, allowing intimate contact of solution with solid surfaces for extended periods of time (days and weeks). Column tests measure adsorption of radionuclides under saturated and unsaturated flow conditions. Details of these tests are given by Serne et al. (1973) and in Appendix A.

The purpose of the reported work is to characterize sediments typical of the Hanford site in terms of their sorbing selectivities for specific radionuclides, to evaluate a method of characterizing radiochemical sorption in unsaturated sediments, and to compare this method with the batch K_d method. Since chemical and physical properties of the geologic materials as well as solution chemistry are known to significantly affect radionuclide transport, the results reported are specific to the materials, solutions, and radionuclides tested. The results, however, illustrate the major differences in technique required to assess saturated and unsaturated radionuclide transport.

MATERIALS AND METHODS

SOILS

Two contrasting materials, designated as Soil A and Soil B, were used in the laboratory tests. Soil A is subsoil material taken from the Ringold geologic formation (Lindberg and Bond 1979). This material is typical of the silty sediments that lie beneath the sands and gravels at a number of waste burial grounds at the Hanford Site. Soil B is a surface soil, of eolian origin, classified as a Rupert sand (typic torripsamment) and is one of the most extensive soils found on the Hanford Site (Hajek 1966). Characterization of these materials followed procedures described by Serne et al. 1973 (also see Appendix A). Measured characteristics included particle size, water retention, water conductivity, mineralogy, organic carbon, cation exchange capacity, exchangeable cations and saturated paste chemistry.

TRACERS

Several radionuclide tracers were selected for the study. These included ^3H , $^{95\text{m}}\text{Tc}$, ^{125}I , ^{85}Sr , ^{137}Cs and ^{60}Co . For some batch tests and all column tests, cobalt was complexed with ethylenediamine tetraacetic acid (EDTA). This complex is hereafter designated as $^{60}\text{Co-EDTA}$. Concentrations of the nuclides used in the tests are listed in Appendix A. For initial runs with the unsaturated columns, a nonradioactive chloride, ^{36}Cl , was used as a tracer.

TESTS

Batch Kd equilibrium tests followed procedures of Serne et al. (1973). Basically, soil was equilibrated with a solution containing the radionuclide and the amount of radionuclide lost from solution was measured. Contacting solutions were characterized for their macro-ion composition. Sorption tests were run for 7, 8.5 and 21 days. Linear adsorption was assumed for all tests. Saturated column tests followed the procedure of Serne et al. (1973). Unsaturated column tests followed procedures of van Genuchten and Wierenga (1977).

Effluent solution was analyzed for tracer activity and the resulting breakthrough curves were in turn used to analyze for the adsorption coefficient, K_d . Details of the procedures for batch method and unsaturated column tests are outlined in Appendix A. Appendix B details the theoretical development of the unsaturated K_d analysis.

RESULTS AND DISCUSSION

Soil characteristics important to radionuclide transport are shown in Tables 1 and 2 and Figures 1 and 2. Since the characteristics of Soil B are more typical of the burial ground soils at Hanford (Routson and Fecht 1979), the majority of the laboratory tests were run using Soil B. The coarse nature of Soil B is reflected in its low cation exchange capacity (Table 1), low silt and clay percentages (Figure 1), low water holding capacity (Figure 2) and relatively low hydraulic conductivity at -0.1 bar, i.e., field capacity (Table 2). The major similarity between the two soils is their clay mineralogy. X-ray analysis shows Soils A and B have similar clay minerals but that they differ in degree of crystallinity and relative amounts. Soil A clay is predominately well crystallized smectite with minor amounts of mica and kaolinite. Soil B consists of poorly crystallized smectites with minor amounts of mica and kaolinite. Amorphous material most likely constitutes the highest proportion of Soil B's total clay make-up. This may not be true for Soil A. The direct influence of these mineralogical differences on radionuclide transport is unclear. However, based on the greater clay fraction percentage, it would be expected that Soil A would exhibit the greater sorption, all other considerations being equal.

Table 1 provides the necessary parameters for modeling the chemistry (ion exchange, complex formation, and precipitation-dissolution) controlling the macro constituents of the soil solution (Routson and Serne 1972). Also, predictions of unsaturated water flow can be made from a knowledge of the soil hydraulic properties and climatic variables (Gee and Simmons 1979). The coupling of the chemistry with the unsaturated water flow to predict radionuclide transport in the unsaturated zone depends highly on the reliability of the batch K_d measurements to predict sorption in unsaturated sediments.

TABLE 1. Soil Characteristics

Characteristic	Value	
	Soil A	Soil B
Saturated paste pH	8.8	8.2
Moisture % at saturation	34.0	21.10
Saturated paste composition, ppm		
Na ⁺	149	9
K ⁺	1.8	5.6
Ca ⁺⁺	25	37
Mg ⁺⁺	4.4	5.6
Cl ⁻	30.4	0.8
SO ₄ ⁼	185	7.5
NO ₃ ⁻	2.7	6.4
CO ₃ ⁼	10	5.0
HCO ₃ ⁻	179	133.1
Cation exchange capacity, meq/100 g	12.0 ± 0.1	5.0 ± 0.1
Distribution on exchange, meq/100 g		
Ca ⁺⁺	6.6 (55%) ^(a)	3.5 (70%)
Mg ⁺⁺	3.8 (32%)	1.0 (20%)
K ⁺	0.2 (1%)	0.4 (8%)
Na ⁺	1.4 (12%)	0.1 (2%)
Calcium carbonate content, %	1.38 ± 0.17	0.07 ± 0.02
Organic carbon content, %	0.14 ± 0.0	0.10 ± 0.00
Particle size distribution, %		
Sand	45	87
Silt	44	9.3
Clay	11	3.7
Clay mineralogy	Smectite, minor amounts of mica and trace of kaolinite	

(a) Number in parentheses is the percent of total cation exchange capacity

TABLE 2. Water Conductivity of Sediments A and B as a Function of Soil Matric Potential (after method of Campbell 1974)

Matric Potential, -bars	Soil A, cm/min	Soil B, cm/min
0 (saturated)	2.0×10^{-3}	1.1×10^0
0.1	3.6×10^{-4}	1.2×10^{-5}
0.3	2.8×10^{-5}	3.5×10^{-6}
0.5	1.4×10^{-6}	1.9×10^{-6}
1.0	1.7×10^{-7}	1.2×10^{-6}
5.0	5.7×10^{-9}	6.9×10^{-7}
10.0	2.4×10^{-9}	5.7×10^{-7}
15.0	6.4×10^{-10}	3.2×10^{-7}

FIGURE 1. Summation Percentage Curves for Hanford Sediments Used in Saturated and Unsaturated Kd Tests

FIGURE 2. Water Retention Characteristics for Hanford Sediments

BATCH K_d TESTS

Screening Test 1. - Tc, Sr, and Cs. Six synthetic ground waters were initially prepared for contact with each sediment (Table 3). The first solution contacting each sediment had the composition of the saturation extract. This composition represents the ground water that would first occur when water saturates the arid sediments under study and begins to percolate. The second solution, a 5-to-1 dilution of the saturated extract, represents a scenario in which a large amount of water contacts the arid sediment, dissolves all the evaporates, and percolates through the sediment. The third solution was five times as concentrated as the saturation extract. If unsaturated conditions prevail in the sediment, percolating waters could dissolve large amounts of

TABLE 3. Composition of Solutions Contacting Sediments

Solution	Na	K	Ca	Mg	HCO ₃	CO ₃	SO ₄	Cl	NO ₃
ppm									
Soil A									
1	113	1.2	15	3.6	80	10	200	8	2
2	17	0.6	9	1.8	31	0	39	2	0.5
3	550	6.2	49	12.6	232	50	950	34	13
4	138	1.3	30	5.1	---	---	---	271	---
5	26	0.4	11	2.1	---	---	---	57	---
6	760	6.7	126	18.3	---	---	---	1485	---
Soil B									
1	5.8	3.7	4.2	3.4	32	8	7	0.5	6
2	1.0	1.1	4.1	1.3	16	0	4.5	0.5	1
3	23	17	6.4	11.3	80	24	36.5	0.8	32
4	7.4	1.2	38	5.6	---	---	---	99	---
5	1.8	0.6	8	1.3	---	---	---	21	---
6	46	6.2	185	22.6	---	---	---	474	---
H	3450	5860	400	---	---	---	---	---	19,830
L	3450	390	80	---	---	---	---	---	10,170

evaporites and build up salt concentrations greater than the saturated extract. The fourth, fifth, and sixth solutions are similar to the first three solutions except that the anion contents were satisfied by using chloride. The fourth through sixth solutions were used to simplify the experiments by minimizing complexation of the cations with bicarbonates-carbonates and sulfates. The intention was to simplify the chemical reactions occurring and allow cation competition effects to be isolated and studied. For the concentrated solutions representing five times the saturation extract, precipitates formed, lowering the total dissolved salt concentration. Table 3 shows the measured concentrations of the synthetic ground waters. Two additional solutions were used to contact Soil B. These were designated as high (H) and low (L) salt solutions and were composed of nitrate salts in the proportions shown in Table 3. The high and low salt solutions were used extensively in the unsaturated column studies.

The distribution (adsorption) coefficients (K_d) for technetium, strontium and cesium for the various solutions contacting Soils A and B were determined in triplicate initially for two contact times, 8.5 days and 21.5 days. The pH's of the solutions were measured at these times also. Table 4 lists the average values for the K_d s and pHs.

The negative K_d values for technetium are an artifact of the calculation scheme. They represent cases in which the average activity in blank tubes (without sediments) is less than the activity in the sediment suspension effluents. Negative K_d values occur only in systems in which sediment sorption is extremely low. In this circumstance, the effluent and influent activities are nearly equal, which means that counting techniques become very important. In the calculation of K_d the effluent is subtracted from the influent, and similar values can lead to a negative difference. For transport calculations, a negative K_d value should be equated to zero and thus the radionuclide should travel at the same velocity as the water. The very low technetium adsorption occurs because the technetium species, which is stable in the Eh-pH field common for shallow land burial sites, is the pertechnetate anion (TcO_4^-). Sediments low in organic content commonly have very low anion exchange capacity and allow anions to percolate relatively unimpeded. It is possible that some of the negative K_d values for technetium are caused by anion exclusion by the inner surfaces of the clay minerals present in the sediments. The data in Table 4 show no relationship between different solution compositions, pHs or contact times and the $K_{d_{\text{Tc}}}$. There is also no significant difference in $K_{d_{\text{Tc}}}$ for the two sediments studied. Similar results on Hanford sediments for technetium have been reported by Barney (1979).

The strontium sorption data show that high sorption occurs on both sediments for the saturation extract solutions. The first three solutions, which include anions capable of forming soluble complexes with strontium, show greater sorption than the three chloride solutions. This has been observed for other sediments and may reflect strontium exchange with calcium in precipitates such as CaCO_3 . It is also known that strontium sorption increases with

TABLE 4. Batch Kd and pH Values for Technetium, Strontium and Cesium on Soil A and Soil B

Solution	Kd _{Tc}		Kd _{Sr}		Kd _{Cs}		pH	
	8.5 Days	21.5 Days	8.5 Days	21.5 Days	8.5 Days	21.5 Days	8.5 Days	21.5 Days
Soil A								
1	-0.38 ± 1.51	-2.77 ± 0.23	133 ± 13	112 ± 1	5307 ± 100	13,525 ± 4,741	8.13 ± 0.11	8.26 ± 0.03
2	-0.88 ± 0.52	-1.13 ± 2.38	238 ± 21	181 ± 12	3377 ± 1311	6,432 ± 1,219	7.95 ± 0.09	8.07 ± 0.03
3	-1.36 ± 0.71	-0.04 ± 0.21	40 ± 3	38 ± 8	3730 ± 1387	7,298 ± 1,098	8.60 ± 0.01	8.52 ± 0.11
4	0.41 ± 0.34	0.57 ± 0.17	86 ± 8	74 ± 3	8832 ± 3417	8,217 ± 2,380	7.56 ± 0.02	7.78 ± 0.03
5	-2.34 ± 0.98	0.54 ± 0.65	222 ± 28	207 ± 18	5995 ± 3632	6,033 ± 1,534	7.72 ± 0.02	7.90 ± 0.02
6	-0.81 ± 0.39	-0.51 ± 1.20	17 ± 1	21 ± 3	4233 ± 1321	11,522 ± 2,154	7.65 ± 0.03	7.75 ± 0.03
Soil B								
1	0.54 ± 1.61	0.07 ± 0.32	129 ± 15	114 ± 9	2042 ± 401	1,505 ± 320	7.50 ± 0.09	8.14 ± 0.02
2	-0.02 ± 0.99	-1.62 ± 0.60	170 ± 27	132 ± 11	1388 ± 226	1,094 ± 295	7.46 ± 0.04	8.00 ± 0.02
3	-0.85 ± 0.32	-0.31 ± 0.30	31 ± 3	38 ± 1	2291 ± 819	3,016 ± 722	7.25 ± 0.05	8.25 ± 0.08
4	1.27 ± 1.67	0.06 ± 0.68	47 ± 4	39 ± 2	3405 ± 1215	5,805 ± 2,109	8.08 ± 0.01	7.63 ± 0.11
5	-0.96 ± 0.37	0.52 ± 0.51	36 ± 2	37 ± 1	5708 ± 2635	3,045 ± 377	7.91 ± 0.01	7.57 ± 0.05
6	-0.09 ± 0.76	0.38 ± 1.23	9 ± 3	12 ± 2	3215 ± 470	3,253 ± 80	8.31 ± 0.06	7.44 ± 0.02

increasing solution pH. The simulated saturation extracts averaged 0.3 to 0.9 pH units larger than the chloride solutions. This might partially explain the greater sorption of strontium. For both sediments, the K_d for strontium shows significant cation competition effects. The sorption of strontium decreases as the cation content of solutions increases, as would be expected from simple ion exchange theory. Soil A, with more fine material and a larger cation exchange capacity (see Table 1), shows higher K_d for strontium, which would be expected from ion exchange principles. Strontium sorption appears to be complete after 8 days and from other experiments on Hanford sediments has been found to reach steady-state within 48 hr (Serne et al. 1973).

For both sediments, the cesium sorption data show very high sorption for all the solutions studied. The sorption of Cs on Soil A appears to be time dependent. For all other radionuclides the 8.5 day equilibration appears to be adequate. Apparently no significant cation-competition effects occurred between the solutions. All solutions show very high sorption. For Soil B the simulated saturation extract solutions show lower K_d values for cesium than do synthetic solutions containing only chloride. This suggests possible formation of soluble complexes. Cesium is not known to form any strong complexes with bicarbonate, carbonate or sulfate anions; therefore the observed differences cannot readily be explained. The very large sorption of cesium and the lack of ion exchange-like cation competition suggest that the clay material (especially the mica) may be preferentially fixing the cesium. The reversibility of the cesium sorption should be investigated because illitic clays are known to irreversibly fix cesium so that it desorbs very slowly and only partially.

The screening experiments suggest:

- Anions will move as rapidly as water through the Hanford sediments under shallow land burial conditions.
- Strontium sorption is controlled by ion exchange-like reactions and can be modeled by the techniques described by Routson and Serne (1972).

- Cesium is very strongly bound under the conditions studied and probably will not be transported more than a few feet before decaying to undetectable levels. It also appears that the methods described by Routson and Serne (1972) should not be used for this particular study to generate $K_{d_{Cs}}$ data needed for transport models.

From the radionuclide sorption screening experiments, one can estimate that:

- Elements such as technetium, iodine, and antimony might be mobile (move at the speed of the carrier water).
- Strontium would be retarded significantly (move about 250 times slower than water).
- Cesium could be extremely retarded (move about 3000 times slower than water).
- Rare earths such as europium, cerium, praseodymium, and samarium would be retarded significantly by precipitation reactions; i.e., at alkaline pHs, rare earths are very insoluble.

Screening Test 2. Seven Day Equilibration - Tc, Sr, Cs, Se, I, and Co.

Batch Kd tests were run with B soil material using a 7 day equilibration time. Table 5 shows the results of the batch experiments using the solutions listed in Table 3.

TABLE 5. Batch Kd Values for Soil B

Solution	Seven Day Values, (ml/g + Standard Deviation)						
	Radionuclide						
	^{95m}Tc	^{85}Sr	^{137}Cs	^{75}Se	^{125}I	$^{125}I-EDTA$	^{60}Co
1	--	--	--	27 ± 2	7 ± 2	--	4570 ± 650
2	--	--	--	26 ± 2	9 ± 1	--	2750 ± 200
3	--	--	--	16 ± 3	11 ± 3	--	3670 ± 160
4	--	--	--	38 ± 12	15 ± 5	--	11070 ± 6480
5	--	--	--	40 ± 2	10 ± 4	--	2735 ± 490
6	--	--	--	72 ± 10	4 ± 2	--	4090 ± 620
L	-3 ± 2	6 ± 1	268 ± 4	--	18 ± 22	4 ± 3	--
H	-1 ± 0.3	1 ± 0.2	25 ± 1	--	4 ± 6	-2 ± 4	--

Tc - Technetium exhibited the same low sorption response as previously noted.

Sr and Cs - The high concentration salt solutions, L and H, show reduced sorption of strontium and cesium as expected from ion exchange and mass action effects.

Se - Selenium appears to be only moderately sorbed onto Soil B. In contrast to strontium, the Kd_{Se} values show little dependence on solution cation concentrations.

I - Iodine sorption data were somewhat inconsistent. For both the high concentration salt solutions (L and H) the results indicated that sorption of ^{125}I occurred from the test solutions. However, a large coefficient of variation was observed for these tests and suggested that additional work would be necessary to delineate the magnitude of the sorption of iodine in Soil B. The addition of ethylenediamine tetraacetic acid (EDTA) to the ^{125}I -spiked solution had the apparent effect of reducing the Kd values for both the high and low salt solution tests.

Co - A clear demonstration of the effects of EDTA on radionuclide mobility is illustrated by the Kd_{Co} data. For the solutions tested, the Co-EDTA complex is mobile (Kd values near zero) while the uncomplexed cobalt is strongly sorbed to the Soil B (Kd values over 1000). Means et al. (1978) observed migration of EDTA complexed cobalt from low level waste disposal pits at Oak Ridge National Laboratory burial grounds. The EDTA-induced reductions in Kd_{Co} values reported by Means et al. (1978) are very similar to those we report here (Table 5). It is clear that the presence of complexing agents such as EDTA will play a major role in determining the transport of cobalt and similar radionuclides at waste burial sites.

Additional 7-day batch Kd tests for iodine were run on Soil B. Table 6 shows results of batch tests in which the iodine solution concentration was increased from less than 1 ppb to 20 ppb. As the iodine concentration was increased, the Kd_I values became less erratic and decreased from 18 ml/g to less than 1 ml/g. The values at 20 ppb iodine are comparable to those observed for tritium on the same soil material (Table 6). The data indicate that iodine

TABLE 6. Batch Kd Data for Iodine and Tritium for Soil B.
Equilibration time was 7 days.

Radionuclide	Solution	Kd, ml/g	pH
¹²⁵ I			
1. <1 ppb ¹²⁵ I	H ^(a)	4 ± 6	---
	L	18 ± 22	---
2. <1 ppb ¹²⁵ I	H	2.5 ± 0.3	7.7
plus 1% phenol	L	2.8 ± 0.2	8.2
3. 5 ppb ¹²⁵ I	H	0.08 ± 0.6	8.0
4. 20 pspb ¹²⁵ I	H	0.05 ± 0.4	8.0
	L	0.05 ± 0.2	8.4
5. 20 ppb ¹²⁵ I	H	0.1 ± 0.4	7.9
plus ⁶⁰ Co-EDTA			
Tritium	H	0.1 ± 0.3	8.1
	L	0.4 ± 0.5	8.4

(a) See Table 3 for solution composition

is mobile at concentrations above 5 ppb. At lower concentrations, the Kd_I values are significantly greater than zero. The sorption mechanism for iodine on this soil is not known. Less than 0.1% organic matter is present in Soil B and the technetium data suggest little evidence of anion exchange.

The improvement in precision by addition of phenol to the solution at the lowest ¹²⁵I concentration suggests the possible influence of microbial activity on the Kd measurements. Results from unsaturated column studies, described later, also reveal that a nonexchangeable sorption mechanism is operating at low iodine concentrations. These data indicate that a critical concentration exists for iodine, below which iodine can be immobilized. Immobilization of iodine is apparent in Soil B at concentrations below 5 ppb (Table 6).

SATURATED COLUMN TESTS

Several saturated columns were run in preliminary tests to assess the mobility of radionuclides through Soil B. Tc, Sr, Cs were applied as a two pore volume pulse to the influent of the saturated flow column at a flow rate of 23 cm/day. When the low salt (L) solution was used, technetium and strontium breakthrough was observed, but no cesium was observed, even at 130 pore volumes of effluent. For the high salt (H) solution, breakthrough occurred at 0.5, 2 and 25 pore volumes for technetium, strontium and cesium, respectively. The retardation of the breakthrough compared qualitatively with the observed Kds of 0, 1 and 25 for technetium, strontium and cesium, respectively (Table 4). The data also showed evidence of solute dispersion. The higher the Kd, the more disperse the breakthrough; hence the lower the observed maximum concentration. Measurable radionuclide concentrations above background occurred for 8, 34, and 90 pore volumes for the 2 pore volume pulse of technetium, strontium and cesium, respectively. This spreading of the peak concentration has significant consequences in assessing the effect of burial ground leachate on ground water contamination (Nelson 1978).

UNSATURATED TRANSPORT

For arid region burial sites, saturation of sediments is seldom obtained, hence leaching rates are low. Sorption of the radionuclide by the soil to any measurable extent will have the effect of even further reducing the effective solute (nuclide) flux. A simplified expression for solute travel for steady flow, assuming no dispersion, can be expressed as :

$$v_s = v_w / (1 + \rho K_d / \theta) \quad (2)$$

where

v_s = solute flux

v_w = water velocity

ρ = soil bulk density

K_d = adsorption coefficient

θ = volumetric water content.

Figure 3 shows the effect of increasing K_d on the solute travel rates in unsaturated sediments. The flow data are typical of the sandy sediments used for shallow land burial fill material at Hanford. Comparison of wet and drained soil conditions shows the effectiveness of both increased K_d and decreased (drained) water contents on nuclide mobility. Clearly, maintenance of an unsaturated soil is as effective as increasing the sorption capacity of the soil material. For example, the data indicate that the flow velocity of a mobile nuclide (tritium, etc.) at $0.07 \text{ cm}^3/\text{cm}^3$ water content (a typical drained field value for Soil B) is equivalent to the flow of a radionuclide with a K_d of approximately 400 at an intermediate water content of $0.14 \text{ cm}^3/\text{cm}^3$. Except for long-lived radionuclides (half lives >500 years), decay should occur before appreciable movement takes place in Soil B, if the water content is maintained at or below $0.07 \text{ cm}^3/\text{cm}^3$. It should be clear from Figure 3 and the preceding discussion that the unsaturated zone itself acts as a barrier to radionuclide migration.

FIGURE 3. Radionuclide Velocity Through Unsaturated Soil as a Function of the Adsorption Coefficient, K_d

UNSATURATED COLUMN K_d TESTS

Table 7 lists the column parameters for the tests run with unsaturated columns. All tracers except cesium were used in the unsaturated flow studies. Only the high (H) and low (L) salt solutions were used in these tests. The initial tests were run with a chloride tracer.

Chloride. Figure 4 is the breakthrough curve for a 0.01 M Cl pulse through B soil at a steady flow of 6.5 cm/day. The curves are typical of those observed later for radionuclides, with the exception that the initial breakthrough of the chloride is earlier than that observed with other tracers. The early arrival of the chloride is attributed to anion exclusion. The nonsymmetrical shape of the breakthrough curve and the subsequent tailing can be adequately explained by dead-end pores or immobile water (see Appendix B). The repeatability of the test suggested that the shape of the curve reflected the combined effects of immobile water as well as solute dispersion and that the analysis of van Genuchten and Wierenga (1977) could be applied to the breakthrough curve data.

K_d Analysis. Curve fitting procedures were applied to analyze the breakthrough curves, and K_d values were obtained from the resultant fitted parameters (see Appendices A and B for details). Figures 5 and 6 show the results of the curve fitting routine, GAUSHAUS (van Genuchten and Wierenga 1977) on breakthrough of ⁶⁰Co-EDTA. It is readily apparent that the five-parameter model describes the experimental data better than the three-parameter model. Subsequent data analysis made use of either a four- or five-parameter model. The four-parameter model used the experimental pulse as a known parameter. Evaluation of the differences between the five-, four-, and three-parameter curve fitting procedures is described in Appendix C. In general there was less than a 10% difference in K_d values between the five- and four-parameter fitting, but as much as 50% difference in K_d values between the five- and three-parameter models.

TABLE 7. Unsaturated Column Tests with Measured Parameters

Date	Column	Soil	Isotope	Solution(a)	Flow Rate cm/day	Pulse Volume, V/Vo	Column Bulk Density, g/cm ³	Water Content, Vo/Vt	Breakthrough Volume, V/Vo, 0.5
8/3/78	I-0	B	Cl	L	6.4	1.44	1.73	0.168	0.77
8/10/78	I-0	B	Cl	L	6.6	1.44	0.73	0.171	0.83
8/21/78	I-1	B	Tc Co-EDTA	L	6.4	1.88	1.73	0.169	0.91 1.22
8/25/78	I-1	B	Tc Co-EDTA	L	6.4	2.86	1.73	0.171	0.87 1.14
10/3/78	I-1	B	I, ^{<1} ppb Sr Co-EDTA	L	6.8	4.31	1.73	0.173	(b) (b) 1.16
10/25/78	I-1	B	I, ^{<1} ppb	H	6.9	4.50	1.73	0.176	(b)
10/27/78	II-1	B	I, ^{<1} ppb	H	6.8	3.04	1.73	0.200	(b)
11/3/78	I-1	B	Sr Co-EDTA	H	6.7	4.17	1.73	0.175	7.14 1.58
	II-1	B	Sr Co-EDTA	H	6.8	3.63	1.76	0.205	5.15 1.28
11/9/78	II-1	B	I, ^{<1} ppb Sr Co-EDTA	H	6.8	3.73	1.73	0.206	(b) 5.04 1.36
11/27/78	I-1	B	H-3	H	6.7	1.31	1.73	0.175	1.00
1/4/79	I-3	B	H-3	L	2.2	1.51	1.71	0.122	1.10
	II-3	B	H-3	L	2.2	1.30	1.71	0.143	0.96
1/11/78	I-3	B	Tc Co-EDTA	L	2.2	2.24	1.71	0.130	1.09 1.25
	II-3	B	Tc Co-EDTA	L	2.2	1.90	1.71	0.152	(b) 1.24

(a) L = low salt, H = high salt. For solution composition see Table 3.

(b) Effluent Concentration, C/Co, did not exceed 0.5 due to sorption.

TABLE 7. (contd)

Date	Column	Soil	Isotope	Solution(a)	Flow Rate cm/day	Pulse Volume, V/Vo	Column Bulk Density, g/cm ³	Water Content, Vo/Vt	Breakthrough Volume, V/Vo, 0.5
2/1/79	I-3	B	H-3	L	49.3	1.82	1.71	0.214	1.17
	II-3	B	H-3	L	47.9	1.66	1.71	0.225	1.10
2/6/79	I-3	B	H-3	L	48.5	1.80	1.71	0.221	1.20
	II-3	B	H-3	L	49.0	1.79	1.71	0.212	1.10
2/8/79	I-3	B	Tc Co-EDTA	L	48.6	2.61	1.71	0.213	1.10 1.37
	II-3	B	Tc Co-EDTA	L	49.3	2.47	1.71	0.221	1.00 1.37
2/12/79	I-3	B	I, <1 ppb 1% phenol	H	6.7	1.35	1.71	0.177	(b)
	II-3	B	I, <1 ppb 1% phenol	H	6.4	1.08	1.71	0.202	(b)
2/26/79	I-4	B	I, 20 ppb 1% phenol	H	6.6	1.23	1.74	0.182	1.05
	II-4	B	I, 20 ppb	H	6.5	1.19	1.75	0.200	1.04
3/14/79	I-5	A	H-3	L	1.8	1.45	1.37	0.402	1.17
	II-5	A	H-3	L	1.8	1.52	1.36	0.379	1.16
3/21/79	I-5	A	Tc Co-EDTA	L	1.8	1.68	1.41	0.405	(b) 2.15
	II-5	A	Tc Co-EDTA	L	1.8	1.78	1.41	0.391	1.00 2.15
4/4/79	I-6	B/A	H-3	L	1.9	1.54	1.55	0.273	1.20
	II-6	B/A	H-3	L	1.9	1.48	1.55	0.285	1.20
4/17/79	I-6	B/A	I, 20 ppb Co-EDTA	L	1.9	1.93	1.55	0.278	1.17 2.20
	II-6	B/A	I, 20 ppb Co-EDTA	L	1.9	1.94	1.55	0.288	1.12 2.12

(a) L = low salt, H = high salt. For solution composition see Table 3.

(b) Effluent concentration, C/Co, did not exceed 0.5 due to sorption.

FIGURE 4. Relative Salt Concentrations in Effluent of Partially Saturated Soil B Column

FIGURE 5. Breakthrough Curve for Co-EDTA in Soil B at 46% Saturation Using a Three-Parameter Model

FIGURE 6. Breakthrough Curve for Co-EDTA in Soil B at 46% Saturation Using a Five-Parameter Model

Unsaturated K_d values for 13 data sets are presented in Table 8. The flow rates for these tests were all between 6.5 and 6.9 cm/day. K_d values ranged from -0.013 for chloride to 0.75 for strontium. It appeared from inspection of the breakthrough curves that a correlation existed between K_d values and the breakthrough curve pore volume at $C/C_o = 0.5$ as chromatographic theory predicts. Table 9 shows the correlation between the calculated K_d and the breakthrough curve midpoint. Linear regression of K_d on breakthrough indicated there was a sufficiently high correlation, $r^2 = 0.977$, that the linear regression data (Table 9) were used subsequently to estimate the K_d values for other data sets where the GAUSHAUS routine had not been used.

Table 10 shows the comparison of K_d values calculated by the linear regression equation (Table 9) and those obtained by the batch method. The column K_d s tend to be slightly lower than the batch K_d values. They also are more repeatable. The data suggest that for low sorbing radionuclides, the column data provide the more reproducible results.

TABLE 8. Calculated Parameters for Tracer Displacements Through Soil B

Tracer	θ cm ³ /cm ³	q cm/day	R	P	β	α	K _d
³ H	0.175	6.7	1.114	111	0.857	0.496	0.011
Cl	0.163	6.5	0.859	131	0.852	0.476	-0.013
	0.172	6.8	0.921	136	0.847	0.604	-0.008
Tc	0.181	6.9	1.164	50	0.775	0.218	0.017
	0.182	6.9	1.211	47	0.712	0.163	0.022
Co-EDTA	0.181	6.9	2.022	35	0.592	0.235	0.107
	0.182	6.9	2.043	47	0.541	0.241	0.110
Co-EDTA	0.173	6.8	1.377	40	0.805	0.233	0.038
	0.175	6.7	1.857	48	0.820	0.310	0.087
	0.205	6.8	1.568	62	0.744	0.437	0.067
	0.206	6.8	1.786	75	0.708	0.517	0.094
Sr	0.175	6.7	8.44	28	0.721	0.472	0.753
	0.205	6.8	6.36	79	0.657	0.848	0.635

TABLE 9. Comparison of Column Breakthrough Pore Volumes, V/V₀, Evaluated at C/C₀ = 0.5 and Curve Fit K_d Value for Unsaturated Flow Columns of Soil B

Tracer	V/V ₀ , 0.5	K _d
Tritium	1.00	0.011
Chloride	0.77	-0.013
	0.83	-0.008
Technetium	0.91	0.017
	0.87	0.022
Co-EDTA	1.22	0.107
	1.14	0.110
	1.16	0.038
	1.58	0.087
	1.28	0.067
	1.36	0.094
Strontium	7.14	0.753
	5.13	0.635

K_d = 0.1255 (V/V₀)_{0.5} - 0.0877 (linear regression equation)

r² = 0.977

TABLE 10. Comparison of Unsaturated Column and Batch Kd Determinations for Several Radionuclide Tracers on Two Hanford Sediments

Tracer	Soil	Solution	Kd, ml/g	
			Column	Batch
Co-EDTA	B	L	0.07 $\pm$ 0.01	0.1 $\pm$ 1.0
		H	0.09 $\pm$ 0.02	0.9 $\pm$ 1.0
	A	L	0.18	---
Technetium	B	L	0.03 $\pm$ 0.01	-3.0 $\pm$ 2.0
	A	L	0.04	---
Iodine	B	L	---	0.5 $\pm$ 0.2
		H	0.04	0.5 $\pm$ 0.4
	A	L	0.06	0.7 $\pm$ 0.3
		H	---	-0.2 $\pm$ 0.1
Strontium	B	L	---	6.0 $\pm$ 1.0
		H	0.8	1.0 $\pm$ 0.2
Tritium	B	L	0.05	0.4 $\pm$ 0.5
		H	0.04	0.1 $\pm$ 0.3
	A	L	0.06	-0.1 $\pm$ 0.7
		H	---	-0.1 $\pm$ 0.4

The effects of flow velocity and changing water content were observed for ^{60}Co -EDTA displacement through Soil B. No significant differences were observed between the Kd measured at flow rates of 48 cm/day, 2 cm/day and 6.7 cm/day. Since the water content correspondingly dropped from 56% saturation to 31% saturation as Soil B decreased from the highest to lowest flow rates, the data suggest that over a rather wide range of water contents the Kd for Soil B is essentially constant.

Previous work by Routson and Serne (1973) indicated that decreasing water content from saturation to near 50% saturation did not significantly alter the sorption of strontium on sediments similar to B soil. Our extension to lower water contents lends further support to the concept that the saturated (batch or column) Kd values can be used to estimate sorption coefficients in unsaturated soils.

Iodine. The observation of measurable sorption of ^{125}I in the batch experiments was confirmed in the column tests. Figure 7 shows the breakthrough curves for ^{125}I at two concentration levels and with the addition of a 1% phenol solution. The data suggest significant sorption for the <1 ppb iodine (I) concentration while a normal breakthrough curve was observed for 20 ppb iodine. The mechanism for the strong sorption at low concentrations is still not known. Microbial plate counts taken from the phenol and nonphenol <1 ppb I solutions showed no significant difference between them, suggesting that insufficient phenol may have been added. In any case, increasing the I concentration level to 20 ppb eliminated the sorption effects.

FIGURE 7. Breakthrough Curves for ^{125}I Through Soil B at the Indicated Concentration Levels and Treatments

The consequence of these observations is that iodine may be immobilized at shallow land burial sites if the concentration is in the low ppb range.

Layered Columns. Tests run with layered columns (Soil B over A) showed sorption characteristics similar to the A soil in all cases. For ^{60}Co -EDTA the K_d for Soil A was twice that of B. For other radionuclides, including tritium and iodine, there was little difference in the K_d values for Soils A and B.

The calculated column K_d of the A soil was only slightly higher than that of the layered column. The data suggest that soil layering produces a sorption characteristic that reflects the influence of the layer with the highest sorption selectivity. Additional data would be required to test the effect of various layer thickness and layer combinations on the overall column sorption. However, as a first approximation, layered data could be treated as a series resistance network with the K_d of the various layers being the resistance analog, as suggested by Selim et al. (1977).

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APPENDIX A

METHODS

APPENDIX A

METHODS

PHYSICAL AND CHEMICAL CHARACTERIZATION

Water Content

Water content measurements were taken of the soils. Ten to forty gram samples of air dry soil were weighed and dried in one of two methods: 1) for 24 hours at temperatures between 100 and 110°C (Gardner 1965), or 2) for 15 min in a 650 W microwave oven on high power. The microwave oven was used for those soil samples that had not been contacted with radionuclide tracer solution.

Particle Density

The particle density method was modified slightly from that given by G. R. Blake (1965). Vacuum boiling deaired the water and soil samples, thus eliminating the cooling off periods required by heat boiling. Particle density values were calculated as follows:

$$D_p = \frac{d_w \left[\frac{W_s - W_a}{(1+w)} \right]}{\left[\frac{(W_s - W_a)}{(1+w)} \right] - (W_{sw} - W_w)}$$

where D_p = particle density in g/cm³
 d_w = density of water in g/cm³
 w = gravimetric water content of sample in g/g
 W_s = weight of pycnometer plus soil sample
 W_a = weight of pycnometer plus air
 W_{sw} = weight of pycnometer plus soil and water
 W_w = weight of pycnometer plus water

Particle Size Distribution

Particle size distributions of the sediments were made using a modified version of the Day (1965) hydrometer method. Sodium hexametaphosphate was

used as the dispersing agent. Fifty grams were dissolved in distilled water and diluted to 1 liter. A ten-to-one dilution of this stock solution was subsequently used in the tests. Procedure modifications were involved in the mixing step once the sample was in the sedimentation cylinder and in accounting for temperature changes during analysis. A stopper inserted into the mouth of the sedimentation cylinder retained the sample as the cylinder was manually inverted and righted for 30 seconds. Timing began when the mixing was ended. A more thorough mixing was achieved with this method than by using a plunger as suggested by Day.

Corrections for changes in solution viscosity due to changes in temperature were made by taking the temperature and hydrometer reading of a blank concurrently with the sediment samples. The blank consisted of 100 ml of sodium hexametaphosphate solution with distilled water added to make 1 liter. Gee and Bauder (1979), using a simplified equation for the clay fraction, found that soils tested at 1.5 and 24 hr agreed within 0.1 clay percentage units of those determined using a time series and extrapolating the clay (2 μ m) percentage from the summation percentage curve. Our reported results use the Gee and Bauder (1979) modification of the Day method.

Hydraulic Conductivity and Water Retention Characteristics

Hydraulic conductivity values for unsaturated sediments were obtained from measurements of water retention characteristics and from measured saturated hydraulic conductivities.

The 0 to 0.1 bar tension values were obtained using hanging water columns (Klute 1965) with fritted glass porous plates. Tension values in the range from 0.1 to 16.0 bars were obtained in a pressure chamber with a ceramic plate extractor using the method of Richards (1965).

Saturated conductivity measurements were made according to Klute (1965). Soil A's finer particle size distribution and therefore lower conductivity required the falling-head method of measurement. The constant-head method was used for Soil B.

Several methods were tested for evaluating unsaturated conductivity in Soil B. A modified Millington and Quirk (MQ) procedure was used for determining unsaturated flow characteristics (Reisenauer 1973). Values were also calculated according to Campbell (1974) and are from the equation:

$$K(\theta) = k_s (\theta/\theta_s)^{2b+3}$$

where k_s = saturated conductivity

θ_s = saturated water content

b = slope of the logarithmic plot of tension versus water content.

Agreement between the MQ procedure and the Campbell method was satisfactory if care was taken in selecting the proper b value.

The method of Bresler et al. (1978) using the advance of the wetting front in a horizontal infiltration soil column was also tested. All three methods gave similar results (within an order of magnitude) when proper matching factors were used. The Campbell method is reported in the main text.

Mineralogy

X-ray diffraction analysis of the sediments was conducted on the clay fractions. A Norelco XRD-5 unit with high voltage generator, a $\text{CuK}\alpha$ radiation source, an X-ray beam collimating system and a detecting and recording system was used following standard procedures (Whittig 1965). Exchange-saturation of the clays was done using magnesium and potassium.

Saturation Extract

Distilled water was added to air dry soil and mixed with a spatula until saturated conditions were reached. At saturation, the paste glistened, flowed slightly, and slid cleanly from the spatula after sitting for an hour (Bower and Wilcox 1965). A subsample of the saturated soil was oven dried to determine the saturation water percentage. The pH of the saturated paste was measured using a Corning pH/reference combination glass electrode. Reference buffer solutions of pH 7 and 10 were used to standardize the pH meter (Peech 1965).

The saturated paste was vacuum filtered to separate the extract solution from the soil. Soluble cation concentrations of calcium, sodium, potassium and magnesium were determined from the extract solution by atomic absorption spectrophotometry. Spectral lines analyzed on the Perkin-Elmer Model 503 spectrophotometer for the cations were:

Calcium	4227 Å
Sodium	5890-5896 Å
Potassium	7665 Å
Magnesium	2852 Å

Soluble anion concentrations were determined using the appropriate colorimetric, turbidimetric and titration method. Chloride was measured amperometrically with a Buchler-Cotlove Model B5950 chloridometer. Sulfate was determined by the barium sulfate turbidimetric method using Hach reagents (Hach Chemical Company 1975). Nitrate was measured using the cadmium reduction colorimetric method using Hach reagents (Hach Chemical Company 1975). Carbonate and bicarbonate were measured by using the phenolphthalein and methyl orange titration end points, respectively (APHA 1975).

Cation Exchange Capacity

Some radionuclides are retained by soils through ion exchange reactions occurring between the soil, the radionuclide and the carrier solution. The total amount of exchangeable cations that a soil can retain is defined as its cation-exchange-capacity (CEC). The method developed by Routson et al. (1973) to determine the CEC of the calcareous, low exchange capacity sandy soils present in the Hanford region was used.

The procedure involved saturating a soil column with a 1 N Sr solution. $\text{Sr}(\text{OAc})_2 - \text{SrCl}_2$ solution, pH 5, was leached through the column to dissolve carbonates. A second aliquot of the solution, adjusted to pH 7, completed the saturation. A dilute Sr solution (0.05 N) tagged with ^{85}Sr was percolated through the column for equilibration. Entrained equilibration solution was removed by vacuum and by washing with dilute alcohol-polyelectrolyte solutions. The soil column and an aliquot of tracer solution were analyzed for their Sr activities. Cation-exchange-capacity (meq/100 g) was calculated from:

$$\text{CEC}(\text{meq}/100 \text{ g}) = \frac{\text{column activity per unit weight of soil (cpm/g)} \times 100}{\text{specific activity of equilibration solution (cpm/meq)}}$$

Exchangeable Cations

The exchangeable cations of calcium, sodium, magnesium and potassium were extracted from 25 g air dry soil samples using 1 N, pH 7 ammonium acetate (Soil Conservation Service 1972). Atomic absorption analysis determined the cation concentrations in the NH_4OAc extract. Since NH_4OAc dissolves free calcium carbonates and overestimates exchangeable Ca in calcareous soils, the sum of the Na, Mg and K concentrations was subtracted from the CEC value to give the Ca concentration in meq/100 g.

Calcium Carbonate and Organic Carbon

The volume of CO_2 evolved when carbonate is treated with acid is a measure of the calcium carbonate content of the soil. Sodium carbonate was used to calibrate the calcimeter used in the volumetric carbonate determination described by Allison and Moodie (1965). The method, applicable to soils low in organic matter, used 4 N HCl and the reducing agent ferrous chloride for reaction with the calcium carbonate to release CO_2 .

Organic carbon was determined using the Walkley-Black method (Allison 1965). Heat from the addition of H_2SO_4 helped potassium dichromate oxidize the active forms of soil organic carbon. The excess chromate was determined by titration with ferrous sulfate and used to calculate the amount of substances oxidized.

DISTRIBUTION COEFFICIENT (BATCH K_d) PROCEDURE

Determination of a distribution coefficient (K_d) for a radionuclide tracer on a given sediment by the batch method involves the following procedure. A known volume of a real or simulated waste solution is shaken with a known amount of sample until equilibrium or a predetermined time period is reached. The solution contacting the sediment is removed and analyzed. The

ratio of the tracer activity in the sediment to the tracer activity remaining in solution is the Kd value. A description of the experimental technique used in this study is described below.

One-half or one gram samples of sediment less than 2 mm were weighed into tared 50 ml Oak Ridge polycarbonate centrifuge tubes. The samples were rinsed three times using cold (without tracers) synthetic solutions. Each rinse involved shaking on a variable speed linear oscillating shaker overnight, centrifuging at 6,000 rpm for 20 min and discarding the decanted supernatant. Supernatant from the third wash was retained for chemical analysis. Washing was performed to allow the systems to approach equilibrium. The difference between the washed and dry weights was determined to account for the residual solution from the washing process in the Kd calculations.

After tracer nuclides were added to the synthetic solutions, the pH was adjusted and the solution filtered through a 0.45 μ m filter. Tagged solution was added to the centrifuge tubes in a 1:30 solid-to-solution ratio. The same amount of spiked solution was added to centrifuge tubes without sediment and handled similarly. The blank tubes were used to monitor for container sorption. Triplicates of both sample and blank tubes were run. After the samples had shaken for the desired contact period, usually 7 days, pH measurements were taken, the suspensions were centrifuged and aliquots of the supernatants removed and analyzed for nuclide activity. Kd values were calculated using the following equation.

$$Kd_{(\text{nuclide})} = (rCo - Ce)A / CeB$$

where A = amount of tagged solution and residual cold solution, ml

B = total grams of soil present

Ce = concentration of nuclide in effluent solution (cpm/ml)

Co = concentration of nuclide in influent solution (blank activity level, cpm/ml)

r = ratio of tagged solution to total solution, tagged and residual

The reported Kd values are averages of the triplicate samples. Figure A-1 outlines the procedure used.

FIGURE A-1. Batch Kd Procedure Flow Diagram

PARTIALLY SATURATED COLUMNS

Equipment

The experimental equipment for the partially saturated columns was designed after that used by van Genuchten and Wierenga (1977). Influent solutions were applied at the upper end of soil columns packed in plexiglass cylinders of 5.4 cm inside diameter. Columns 27.5 cm long of Soil B were used in all tests, except for the layered soil column tests which are described later. At the lower end of the vertically positioned column, a porous plate for controlling vacuum and supporting the soil was attached. It was made of either 1) Dynapore, a stainless steel porous metal wire mesh (Michigan Dynamics), with a bubbling pressure of about 70 cm, or 2) Spectramesh N Nylon, 30 mesh opening with a bubbling pressure of about 45 cm. Stainless steel wire mesh U.S. Standard Sieve #50 was used for support and protection of the Spectramesh. The column was connected to a vacuum chamber enclosing an automatic fraction collector (Instrumentation Specialties Co., Lincoln, Nebraska).

Vacuum within the soil column was maintained using a Nullmatic differential pressure regulator from Moore Products Co. of Springhouse, Pennsylvania. A step pulse syringe pump with variable speed and time settings (Wierenga et al. 1973) applied the influent solution. Figure A-2 portrays the experimental setup used.

FIGURE A-2. Apparatus for Measuring Solute and Radionuclide Movement in Unsaturated Soil Columns

Packing Procedure

Prior to packing a column the porous plate was saturated using the untagged solution. Height of the sediment within the column was predetermined for column volume calculations. The amount of soil needed to pack the column to the desired bulk density was calculated from:

$$\text{Bulk Density } (D_b) = \frac{\text{oven dry weight of soil}}{\text{volume of soil}}$$

$$\text{Oven Dry Weight} = \frac{\text{air dry weight}}{(1 + w)}$$

where w = the gravimetric water content of air dry soil.

The correct amount of homogeneous air dry Soil B was then hand packed into the column. A long stemmed funnel was used to direct the soil to the bottom of the column. It was slowly raised as the column was filled to the specified height. A tare weight of the column, saturated plate, air dry soil and end stopper was taken to establish the base weight for later water volume calculations.

Tracer Pulse Determination

The tracer nuclides of ^3H , ^{125}I , ^{85}Sr , $^{95\text{m}}\text{Tc}$, and ^{60}Co -EDTA were added to predetermined amounts of the two nitrate salt solutions used in the experiment. The low salt solution consisted of 0.15 M NaNO_3 , 0.01 M KNO_3 and 0.002 M $\text{Ca}(\text{NO}_3)_2$ while the high salt was composed of 0.15 M NaNO_3 , 0.15 M KNO_3 and 0.01 M $\text{Ca}(\text{NO}_3)_2$. Tracer activity levels were 2 pCi $^{125}\text{I}/\text{ml}$, 2 nCi ^{60}Co -EDTA/ml, 2 nCi $^{95\text{m}}\text{Tc}/\text{ml}$, 50 nCi $^{85}\text{Sr}/\text{ml}$ and 0.1 $\mu\text{Ci } ^3\text{H}/\text{ml}$.

Pulse volumes were determined in terms of pore volumes of the specific columns. One pore volume equaled the volumetric water capacity of the soil column. This water capacity was defined as the total amount of water (in milliliters) remaining in the soil column after the column had reached equilibrium or steady state flow conditions. It was determined by weighing the column during the experiment and was the difference from the column's base weight. Larger volumes of tracer solution were made for those nuclides expected to move slower than tritium and technetium.

Experimental Runs

Partially saturated conditions were achieved by initially saturating the column from the bottom up and then draining to the desired level of unsaturation. Water content within the column was controlled by properly adjusting the influent flow rates and vacuum levels obtained from the previously determined hydraulic conductivity data. When the effluent collected at a regular rate, steady state conditions were assumed and the test proceeded. Untagged solution was used during the equilibration process.

Tagged influent was applied until the desired volume had been added. Untagged solution then leached the column until the concentration of the tracer

in the effluent reached less than 1% of the tracer influent concentration and the run was terminated. The rate (flux) of solution passing through the column was computed from measured volumes, times and known cross-sectional areas. Column effluent was monitored for its tracer concentration, total collected volume and rate of collection. Graphs of the relative effluent concentrations and their corresponding pore volumes were plotted. A planimeter was used to graphically determine the percent recovery of the isotopes. Break-through values equal to the pore volumes of effluent with a relative concentration of 0.5 were also determined.

Other column parameters that were measured include pore space, volumetric water content, and percent saturation. Pore space (V_s) within the columns was determined from their bulk density (D_b), particle density (D_p), and volume (V_t) using:

$$V_s = V_t (1 - D_b/D_p)$$

Volumetric water content was the ratio of water in the column to the volume of the column. These were compared to the gravimetric water contents determined when the columns were dissected. Percent saturation, the ratio of the water in the column to the pore space within the column, indicated the degree of column unsaturation.

Layered Columns

Soil A was packed to a 5 cm depth in the same size plexiglass cylinder (5.4 cm i.d.) as used previously. Short columns were used because of the fine texture and low hydraulic conductivity of Soil A. Tritium, technetium and cobalt-EDTA were used in low salt solution runs. Later, five centimeter columns of Soil B were added above the A sediment columns. Experimental runs using tritium, iodine and cobalt-EDTA were completed. Vacuum and influent flow rates were adjusted to maintain steady flow through the A segment of layered column.

TRITIUM COUNTING

Tritium was added to our nitrate salt solutions for an activity of approximately 0.1 $\mu\text{Ci/ml}$ of influent solution. Samples of 250 μl were added to 15 ml of Packard's Insta-Gel, a toluene-based cocktail for aqueous and non-aqueous samples. The samples were temperature equilibrated and their tritium activity determined in a Packard Tricarb Model 3255 liquid scintillation spectrometer. A set of seven quenched tritium standards from Amersham, each with an activity of 5×10^5 dpm in 15 ml of toluene-based cocktail, were used for efficiency determinations. Operation of the machine followed the recommended procedures given in Packard's Instruction Manual 2136 (Packard 1977). Further details were taken from Horrocks' Application of Liquid Scintillation Counting.

External standard ratio (ESR) was used for determining counting efficiency based on the amount of quenching in the sample. Sample ESR values reflected low quenching conditions within the samples. Counting efficiencies were calculated using the following equation:

$$\text{Efficiency} = \frac{\text{CPM (R)}}{\text{DPM}}$$

where CPM (R) = the net counts per minute in the Red Channel

DPM = the activity of the standard in disintegrations per minute.

Plots of the efficiencies of the quenched standards versus ESR were drawn. From these efficiency correlation curves, sample efficiencies were derived. Sample activity was calculated from the ratio of net observed CPM in the Red Channel to the efficiency of that specific sample. Figure A-3 is an external standard ratio efficiency correlation curve for tritium.

GAMMA COUNTING

Samples were counted in a Bicorn 5 in. x 5 in. NaI well with a 5 in. SRC 125B0I bialkali photo-tube attached. Background radiation was shielded out with a steel-lined lead cave. The detector signal was preamplified by an

FIGURE A-3. Tritium Efficiency Correlation Curve

Ortec Model 276 preamplifier. An Ortec active filter pulse shaping amplifier, Model 485, routed the signal to the 100-MHz analog-to-digital converter for pulse-height-analysis in the multichannel analyzer. Output from the Ortec Model 6240B analyzer with 4,096 channel memory identified the chosen regions of interest (ROI) and their contents.

Calibration

Gamma reference sources from New England Nuclear, with energies spanning the range of energies of ^{125}I to ^{60}Co , were used each day to calibrate the counting system. Regions were set around the gamma-ray peaks for the isotopes present by counting standards of the individual isotopes. Standards conformed to the geometry and counting conditions of the samples. Table A-1 lists the energy peaks used for analyzing samples activities.

TABLE A-1. Gamma Energy Peaks Used for Sample Analysis

<u>Isotope</u>	<u>Peak Energy, KeV</u>
^{125}I	27
$^{95\text{m}}\text{Tc}$	204
^{85}Sr	514
^{137}Cs	662
^{60}Co	1,173

Calculations

Background radiation was subtracted from the accumulated counts to give the sample net count. Corrections were then made for the different sample sizes which affect counting efficiencies. The influence of different volumes and container sizes on counting efficiency is depicted in Figure A-4. The corrected net count was computed by:

$$\text{Corrected Net Count} = \frac{\text{Net Count in ROI}}{\text{Volume Efficiency Factor}}$$

where ROI is the region of interest. Whenever all of the samples counted were the same size, no volume corrections were made.

The contribution of each isotope, whenever more than one isotope was added to solution, was accounted for in the activity calculations of the individual isotope. Standard counts and their contributions to the other isotope energy peaks were used to generate matrices. The net samples counts were multiplied by the standard matrix to determine the actual isotope counts. These matrix-corrected values were then reduced to reflect sample sizes. Influent concentrations, C_0 , were computed in the same way.

FIGURE A-4. Sample Volume Efficiency Curves

APPENDIX B

THEORY OF UNSATURATED K_d DETERMINATION

APPENDIX B

THEORY OF UNSATURATED K_d DETERMINATION

Solute transport through porous material can be rigorously described by equations that account for both convection and dispersion. For one dimensional flow, the equation commonly used is:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} - V_o \frac{\partial C}{\partial z} \quad (1)$$

where C is the concentration, D is the dispersion coefficient, V_o is the pore water velocity, z is the distance and t is time. Solutions to Equation (1) predict S-shaped or symmetrical effluent concentration profiles. However, there is a growing body of evidence that in both saturated and unsaturated porous media, asymmetrical concentration curves more typically represent the observed effluent breakthrough (Coats and Smith 1964; van Genuchten and Wierenga 1966, 1977; Gaudet et al. 1977). Coats and Smith (1964) developed transport equations to account for the asymmetry or tailing observed in the effluent curves. Their equations account for diffusion or mass transfer from mobile to immobile regions in the porous material and can be expressed as follows:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} = \theta_m D \frac{\partial^2 C_m}{\partial z^2} - V_m \theta_m \frac{\partial C_m}{\partial z} \quad (2)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} = \alpha (C_m - C_{im}) \quad (3)$$

where the subscripts m and im refer to regions of mobile and immobile water, respectively, where V_m is the pore-water velocity in the mobile region. Equation (3) indicates that a diffusional exchange of material is present between the two regions. It also expresses the proportionality between the exchange rate and the concentration difference between the two regions in terms of α , a

mass transfer coefficient. van Genuchten and Wieranga (1976) have modified Equations (2) and (3) to include adsorption. These equations can be written as follows:

$$\theta_m \frac{\partial C_m}{\partial t} + \theta_{im} \frac{\partial C_{im}}{\partial t} + f\rho \frac{\partial S_m}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} =$$

$$\theta_m D \frac{\partial^2 C_m}{\partial z^2} - \theta_m V_m \frac{\partial C_m}{\partial z} \quad (4)$$

$$\theta_{im} \frac{\partial C_{im}}{\partial t} + (1-f)\rho \frac{\partial S_{im}}{\partial t} = \alpha(C_m - C_{im}). \quad (5)$$

S_m and S_{im} define the adsorption in the mobile and immobile water regions, respectively, and ρ is the soil bulk density. The parameter f characterizes the distribution of adsorption sites into readily accessible sites (f) and sites located in the stagnant region of the soil ($1-f$). Figure B-1 is a schematic diagram of unsaturated sorbing porous material with interaggregate diffusion. van Genuchten and Wieranga (1976) found analytical solutions to Equations (4) and (5), using appropriate boundary conditions, specifying that the adsorption could be described by the Freundlich isotherm as

$$S = K_d C^N \quad (6)$$

where K_d and N are empirical constants. The analytical solutions for linear adsorption ($N = 1$) are described in detail by van Genuchten and Wieranga (1976). A series of important dimensionless variables are defined as follows:

$P = V_m L/D = \text{pecllet number}$

$\phi = \theta_m/\theta = \text{mobile water fraction}$

$\beta = \frac{\theta_m + \rho f K_d}{\theta + \rho K_d} = (\theta_m/\theta)(R_m/R) = \text{dimensionless parameter}$

$R = 1 + \rho K_d/\theta = \text{retardation factor}$

$R_m = 1 + \rho f K_d/\theta_m = \text{mobile water retardation factor}$

$\bar{\alpha} = \alpha L/(V_m \theta_m) = \alpha L/q = \text{dimensionless mass transfer}$

$T = V_o t/L - V_m t \phi/L = \text{pulse volume.}$

FIGURE B-1. Schematic Diagram of Unsaturated Aggregated Porous Medium. (A) Actual Model. (B) Simplified Model. The shading patterns in A and B represent the same regions. (After van Genuchten and Wierenga 1976)

P , R , $\bar{\alpha}$ and β are unknown parameters that are obtained by fitting the equation containing these terms to the experimental breakthrough curves. The mobile water fraction, ϕ , is obtained from a tritium breakthrough curve, assuming $f = 0.5$. It is used with subsequent breakthrough curves of other sorbing solute species, for the same flow conditions, to determine α , D and f for the column. K_d , the linear adsorption coefficient, is determined from the equation

$$K_d = (R-1)\theta/\rho. \quad (7)$$

van Genuchten and Wierenga (1976) have shown that the shape and displacement of the effluent concentration curve is most strongly dependent upon K_d and α , and least dependent upon the dispersion coefficient D . Hence, their results suggest that appropriate analysis of the effluent concentration (breakthrough) curves should yield reliable estimates of the linear adsorption coefficient, K_d .

APPENDIX C

UNSATURATED COLUMN PARAMETER CALCULATIONS

APPENDIX C

UNSATURATED COLUMN PARAMETER CALCULATIONS

Using the data provided on effluent concentrations, three successive parameter optimizations were carried out. We employed an improved version of the curve fitting procedure, GAUSHAUS, used previously by van Genuchten and Wierenga (1976). The column was 27.6 cm long and filled with soil to a bulk density 1.73 g/cm^3 . The fluxes, water contents, and pulse lengths for each experiment are presented in Table C-1. A five parameter curve fitting program was used first by fitting the data as received. The pulse length was optimized, also, except for tritium. In the latter case, the pulse length supplied with the data was used. In an effort to improve the curve fitting, all data were plotted by hand and a smooth curve drawn (eyeball fit) through the data. Data points were taken from this smoothed curve and used as input for a second GAUSHAUS curve fitting. In this second try, the pulse length given in Table C-1 was used, and a 4-parameter curve fitting was performed. A third try was made on the hand-smoothed data. For the third try, it was assumed that the Peclet number was the same for all experiments, and had a value of 85. For pulse lengths the values presented in Table C-1 were taken again. The program was set to optimize for three parameters only (e.g., retardation factor, beta, and alpha bar).

TABLE C-1. Fluxes, Water Contents and Pulse Length During Solute Displacement Experiments

<u>Set</u>	<u>Tracer</u>	<u>Water Content, cm³/cm³</u>	<u>Saturation, %</u>	<u>Flux, cm/day</u>	<u>Pulse PV</u>
0	Tritium	0.175	44.5	6.66	1.31
1	Chloride	0.165	42.0	6.47	1.44
2	Chloride	0.171	43.5	6.82	1.44
3	Technetium	0.181	46.1	6.86	1.88
3	Cobalt-EDTA	0.181	46.1	6.86	1.88
4	Technetium	0.182	46.3	6.89	2.86
4	Cobalt-EDTA	0.182	46.3	6.89	2.86

The results of the three successive curve fits are presented in Table C-2. The first row for each tracer presents the results of the 5-parameter fit, the second row the results of the 4-parameter fit (pulse length given), and the third row the results of the 3-parameter fit (peclet number and pulse length given).

TABLE C-2. Values of Parameters as Determined with a 5-, 4- or 3-Parameter Curve Fitting Program

<u>Set</u>	<u>Tracer</u>	<u>Peclet</u>	<u>Retardation</u>	<u>Beta</u>	<u>Alpha Bar</u>	<u>Pulse PV</u>
0	Tritium	110.6	1.114	0.857	0.496	1.296
		106.4	1.100	0.859	0.445	1.313 ^(a)
		85 ^(a)	1.099	0.872	0.351	1.313 ^(a)
1	Chloride	131.1	0.859	0.852	0.476	1.459
		133.7	0.855	0.853	0.528	1.44 ^(a)
		85 ^(a)	0.852	0.878	0.350	1.44 ^(a)
2	Chloride	135.7	0.921	0.847	0.604	1.43
		126.1	0.913	0.843	0.652	1.44 ^(a)
		85 ^(a)	0.910	0.869	0.448	1.44 ^(a)
3	Technetium	50.2	1.164	0.775	0.218	1.874
		52.8	1.174	0.752	0.211	1.88 ^(a)
		85 ^(a)	1.141	0.754	0.292	1.88 ^(a)
3	Cobalt-EDTA	35.3	2.022	0.592	0.235	1.874
		34.8	1.990	0.584	0.229	1.88 ^(a)
		85 ^(a)	1.745	0.635	0.374	1.88 ^(a)
4	Technetium	47.8	1.211	0.712	0.163	2.86
		47.1	1.270	0.673	0.172	2.86 ^(a)
		85 ^(a)	1.189	0.704	0.237	2.86 ^(a)
4	Cobalt-EDTA	46.8	2.043	0.541	0.241	2.86
		46.3	1.955	0.552	0.236	2.86 ^(a)
		85 ^(a)	1.880	0.563	0.284	2.86 ^(a)

(a) These parameters were given the indicated value (i.e., they were not optimized).

The data in Table C-3 show that smoothing of the input data had little effect on the values of the parameters found with the curve fitting program. The 95% confidence limits for the peclet number for the tritium experiment were 86.2 and 126.6, respectively. As a first approach it may be assumed that the peclet number for each experiment should be the same. Therefore, the curve fitting was repeated, taking for peclet number the lower limit of the 95% confidence interval from the tritium experiment (e.g., 85). The results are presented in Table C-2. As might have been expected from the correlation matrices for each experiment, changes in peclet number had a relatively minor effect on the retardation factors (except for cobalt) but quite an effect on the alpha bar values.

TABLE C-3. Values for Phi, Alpha, K, f and D Derived from Table C-2

<u>Set</u>	<u>Tracer</u>	<u>ϕ</u>	<u>D, cm²/day</u>	<u>α, 1/day</u>	<u>Kd, ml/g</u>	<u>f</u>
1	Tritium	0.898	10.6	0.120	0.011	0.5
		0.895	11.1	0.107	0.010	0.5
		0.909	13.6	0.085	0.010	0.5
3	Technetium	0.898	23.2	0.054	0.017	0.025
		0.895	22.2	0.052	0.018	--
		0.909	13.5	0.073	0.015	--
3	Cobalt-EDTA	0.898	33.0	0.058	0.017	0.293
		0.895	33.6	0.057	0.104	0.270
		0.909	13.5	0.093	0.078	0.267
4	Technetium	0.898	24.6	0.041	0.022	--
		0.895	24.8	0.043	0.028	--
		0.909	13.5	0.059	0.020	--
4	Cobalt-EDTA	0.898	24.7	0.060	0.110	0.199
		0.895	25.2	0.059	0.105	0.148
		0.909	13.5	0.071	0.093	0.170

The data in Table C-2 were used to compute values for the adsorption coefficient, K_d ; the dispersion coefficient, D ; the mass transfer coefficient, a ; the fraction mobile water, ϕ ; and the fraction of adsorption on "mobile" soil, f . The results are presented in Table C-3. The rows for each tracer in Table C-3 refer to the rows in Table C-2. Calculations were omitted for chloride, which is negatively adsorbed. Use of the mobile-immobile model for chloride has not yet been described adequately. Note that the same fraction mobile water (ϕ) was assumed for all tracers as for tritium.

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