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Radionuclide Distribution Coefficients for Sediments Collected from Borehole 299-E17-21: Final Report for Subtask 1a

D. I. Kaplan
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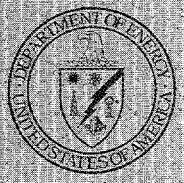
October 1998



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Richland, Washington 99352

Summary

Over 360 distribution coefficients (K_d) for cesium, iodine, selenium, strontium, technetium, and uranium were measured in fiscal year 1998 using 20 sediments collected from borehole 299-E17-21 on the Hanford Site as part of the Immobilized Low-Activity Waste-Performance Assessment (ILAW-PA). Additionally, the pH and cation-exchange capacity (a measure of the total quantity of cations that a sediment can adsorb) of these sediment samples were measured. The sediment samples originated from the Hanford formation (informal name). Statistical analyses, using Student's t-test and correlation, were conducted with the measured values. There were no significant differences between layers 1 and 2 for the selenium, strontium, technetium, and uranium K_d values (statistics could not be applied to evaluate layer 3 K_d values). Significant differences between the cesium and iodine K_d values for layers 1 and 2 were observed. However, these differences were modest and would likely not warrant the added complexity of using three distinct K_d regions to represent the Hanford formation in the ILAW-PA model. Generally, the K_d values of layer 3 were more similar to those of layer 2 than those of layer 1.

Conservative and best estimates of radionuclide K_d values were calculated based on the results from these measurements. The best estimate was chosen to be the calculated median value; whereas the conservative estimate was the minimum value, except for the conservative uranium K_d estimate that was based on the second-to-lowest value because of the presence of an unusually low value that was not consistent with other values from this borehole or previous reported values.

Overall, the estimates are consistent with values used for the ILAW-PA, with some notable exceptions. The conservative K_d estimates for technetium and uranium are approximately the same as those used for the ILAW-PA. The conservative values for cesium, selenium, and strontium were appreciably more conservative than necessary. The conservative iodine value is appreciably less than that used in the ILAW-PA and was based on a literature review of K_d values measured using Hanford Site sediments. The cause for the lower iodine K_d values measured in borehole 299-E17-21 sediments is not known, though the sediments used in this study clearly had appreciably lower concentrations of fine materials than the Hanford Site sediments previously used in iodine sorption measurements. These differences in K_d values underscore the importance of basing K_d estimates for the ILAW-PA on measurements using site-specific sediments.

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1.0 Introduction

Distribution coefficient (K_d) values for cesium (as Cs^+), iodine (as I^-), selenium (as SeO_4^{2-}), strontium (as Sr^{2+}), technetium (as TcO_4^-), and uranium (as UO_2^{2+}) were measured in 20 sediments collected from borehole 299-E17-21 on the Hanford Site by Pacific Northwest National Laboratory.[1] Additionally, the pH and cation-exchange capacity (CEC) of these sediment samples were measured. Statistical analyses, using Student's t-test and correlation, were conducted with the measured values.

1.1 Background

There are two general approaches being taken to understand and predict the behavior of key radionuclides at the Immobilized Low-Activity Waste-Disposal Complex (ILAW-DC) on the Hanford Site. The first approach is to use nearby sediments to determine the conceptual model of radionuclide behavior at the ILAW-DC. The second approach is to use the limited amount of site-specific sediment samples collected from boreholes to provide a quantitative measure of radionuclide geochemical behavior at the ILAW-DC. Ideally, all experiments could be conducted using site-specific sediments because the science of geochemistry is not yet advanced enough to permit estimating the geochemical behavior of a radionuclide in one sediment based on its behavior in another sediment. However, site-specific sediments are generally expensive to collect, and the volume of material available is limited.

Using non-site-specific sediments permits one to conduct experiments that require large amounts of sediment. The sediments used for this study have generally originated from near the 200-East Area on the Hanford Site. These experiments have investigated the effect of the degree of moisture saturation (Kaplan et al. 1996, Gamerdinger et al. 1998), pH (Kaplan et al. 1996, 1998a, 1998b), mobile colloids (McGraw and Kaplan 1997, Lee et al. 1998), ionic strength (Kaplan et al. 1995, 1998b), radionuclide concentration (Kaplan et al. 1996), and sediment properties on the geochemical behavior of key radionuclides (Parker 1997). All these parameters are known to affect sorption of solutes, but the degree to which they do so in Hanford Site sediments, or more specifically in ILAW-DC sediments, is not known.

The most technically defensible way to quantify radionuclide sorption is through experiments conducted with site-specific sediments and pore water or waste leachate. This report describes geochemical characterization and radionuclide K_d measurements made using the first borehole sediments collected from the ILAW-DC (borehole 299-E17-21). The characterization plan for this borehole was presented in Reidel et al. (1998). These sediments were characterized for physical and hydrologic properties by researchers at Pacific Northwest National Laboratory.[2] Also, the results from this report and those in the Fayer et al. letter report will be modeled during fiscal year 1999.

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[1] Pacific Northwest National Laboratory is operated by Battelle for the U.S. Department of Energy.

[2] 1998 letter report, Physical and Hydraulic Measurements of FY 1998 Borehole Cores, M. J. Fayer, A. L. Ward, J. S. Ritter, and R. E. Clayton.

1.2 Objectives and Hypothesis

The hypothesis of this study was that the K_d values of the three geologic layers identified in borehole 299-E17-21 within the Hanford formation were the same. To test this hypothesis, the K_d values of several radionuclides were measured using 20 subsamples from borehole 299-E17-21 (Reidel et al. 1998). Another objective of this study, in addition to resolving the hypothesis, was to measure ancillary chemistry, pH, and CEC of the sediments to provide additional information for interpreting the measured K_d values. The final objective of this study was to provide a measure of the variability of the K_d values within each geologic formation.

1.3 Document Outline

This report is composed of several chapters in addition to this introduction. The materials and methods are given in Chapter 2.0. Chapter 3.0 describes the results and gives the discussion for those results. The conclusions gained from these sediment studies are given in Chapter 4.0, followed by the references cited in the text (Chapter 5.0). The appendix contains statistical information.

2.0 Materials and Methods

2.1 Materials

The sediment samples used in these experiments originated from borehole 299-E17-21. A log of the borehole was presented in Reidel et al. (1998). Selected cores from this borehole were transferred to M. J. Fayer, Pacific Northwest National Laboratory, who is making, concurrent with this study, a number of hydrologic and physical measurements of the same sediments. Sediment samples were measured into test vials directly from the sample bag used by Fayer for his tests. Because the geochemistry and hydrology laboratories are adjacent to each other, there was no need for a chain-of-custody form; the samples were never removed from the hydrology laboratory.

2.2 Methods

Groundwater used in these experiments came from well 699-S3-25, an uncontaminated well located on the Hanford Site (Table 1). It was shown in Serne et al. (1993) that Hanford Site vadose-zone sediment pore waters are quite similar to the underlying groundwater. It is much easier to collect groundwater than vadose-zone pore water. Thus, the adsorption tests were performed with an uncontaminated Hanford Site groundwater. The groundwater was analyzed using standard techniques. Inductively coupled plasma-atomic emission spectroscopy, with an analytical precision of $\leq \pm 4\%$ at 5 mg/L, was used

Table 1. Chemical Composition of Uncontaminated Hanford Site Groundwater (<0.45-μm filter) Used as Background Solution for K_d Measurements

Constituent	Concentration (mg/L)
pH	8.4 (unitless)
Cl^-	24
NO_3^-	1.7
SO_4^{-2}	109
Total organic carbon	0.73
Total alkalinity (as CO_3^{2-})	160
Al	0.14
B	0.05
Ba	0.069
Ca	58
Fe	0.14
K	14
Mg	16
Mn	0.046
Na	30
Si	16.2

to determine dissolved cation concentrations. Ion chromatography, with an analytical precision of ≤±4% at 5 mg/L, was used to determine dissolved anion concentrations. Analysis for ^{99}Tc was by liquid scintillation counting (LSC), using a quench-calibrated Wallac® 1415 LSC and Packard® Opti-fluor™ LSC cocktail (Wallac Instruments, Inc. and Packard Instruments, Meriden, Connecticut). Analysis for ^{137}Cs, ^{75}Se, and ^{125}I was by gamma energy analysis using a Wallac® 1480 Wizard™ 3-in. NaI automatic gamma detector. All radiological measurements were performed to 3% combined error with systematic error accounting for <1% of the total. U(VI) was measured by laser phosphorimetry (Chemchek Instruments, Inc., Richland, Washington; Brina and Miller 1992). The laser phosphorimetry method had a detection limit of 0.005 mg/L UO_2^{2+} and an analytical precision of 2% at 0.01 mg/L UO_2^{2+}.

The K_d measurements were made following the procedure described in Relyea et al. (1980). These measurements were made with sediments that had been oven dried at 105°C. The sediments were then preequilibrated in the Hanford Site groundwater (Table 2). This was accomplished by adding groundwater to the sediments, shaking the suspensions overnight, centrifuging, pouring off the supernatant, and then measuring the pH of the supernatant. This was repeated three times. The purpose of this preequilibration step was to isolate the radionuclide adsorption reaction from the large number of other reactions that may occur while sediments and aqueous solutions come to chemical equilibrium. This has been

Table 2. Experimental Conditions for K_d Measurements[(a)]

Radionuclide	Sediment (g/tube)	Liquid (mL/tube)	Spike Solution Activity
^{75}Se, ^{125}I	10	20	15 mCi/mL
U	10	20	200 ppb
^{137}Cs, ^{85}Sr	1	30	25 mCi/mL
^{99}Tc	10	20	10 mCi/mL

(a) Sediments were used as received (i.e., the sediments were not sieved); all measurements included 3 replicates; sediments were preequilibrated with three 1-day washes with Hanford Site groundwater; 14-day contact times with radioisotopes and sediments; positive control = no sediment added + spiked groundwater; negative control = unspiked groundwater and no sediment added.

shown to be a critical step for accurately measuring adsorption values and minimizing precipitation and/or coprecipitation of several radiotracers (Relyea et al. 1980).

Four sets of K_d values were measured using the experimental conditions presented in Table 2. In an effort to increase productivity, ^{125}I (as $^{125}I^-$) and ^{75}Se (as $^{75}SeO_4^{2-}$) were combined in one solution and ^{137}Cs (as $^{137}Cs^+$) and ^{85}Sr (as $^{85}Sr^{2+}$) in another solution. Previous studies have shown that ^{125}I and ^{75}Se (Kaplan et al. 1998b) and ^{137}Cs and ^{85}Sr (Parker 1997) can be placed in the same K_d test tube without interfering with analytical detection or competing for sorption sites on the sediment. Uranium (as UO_2^{2+}) and ^{99}Tc (as TcO_4^-) K_d tests were conducted in systems containing only one radionuclide. The sediment/groundwater slurries were placed on a platform shaker for 14 days, a period selected to ensure that steady-state conditions were achieved. These solutions were then passed though a 450-nm filter. The filtrates were analyzed for radionuclide activity.

A 20- or 30-mL aliquot of the filtered radionuclide solutions was then added to 1 or 10 g of preequilibrated sediment (see Table 2). The radionuclide/groundwater/sediment suspensions were placed on a slow-moving platform shaker for 14 days. This duration was selected to ensure that the system reached steady state. Preliminary experiments showed that uranium and iodide sorption to these sediments remained constant between 2 and 14 days (Kaplan et al. 1996). The suspensions were centrifuged, and the resulting supernatants were then passed through 0.45-μm filters. Radionuclide activity of the filtrates was measured.

The K_ds (mL/g) were calculated using the following equation:

$$K_d = \frac{\left(A_{spike} \times V_{spike}\right) - A_{final}\left(V_{spike} + V_{excess}\right)}{A_{final} \times M_{sediment}} \quad (1)$$

where A_{spike} is the initial radionuclide activity in the spike solution (μCi/L; positive control), V_{spike} is the volume of radionuclide solution (mL), A_{final} is the radionuclide activity in the effluent solution after

equilibration (μCi/L), V_{excess} (mL) is the volume of excess solution left after the third preequilibration wash (weight of excess solution divided by solution density), and $M_{sediment}$ is the sediment mass (g).

The sediment-to-solution ratios were selected to optimize K_d measurements. In the case of the weaker sorbing solutes (Se, I, U, and Tc), a low sediment-to-solution ratio of 1:2 was used. This low ratio was used to improve K_d measurement accuracy. As can be seen from Equation (1), the activity of adsorbed radionuclide is determined by subtracting the radionuclide activity in solution before, A_{spike}, and after, A_{final}, contact with the sediment. If little adsorption takes place, then the difference between A_{spike} and A_{final} will be small. Thus, one of the difficulties in determining low-K_d values is that two large numbers must be subtracted from each other to determine a small value, a poorly poised mathematical situation. To obtain a greater difference between A_{spike} and A_{final}, the ratio of sediment to solution was increased in these tests. In the case of the stronger sorbing solutes (Cs and Sr), a higher sediment-to-solution ratio of 1:30 was used. This higher ratio permits measuring high-K_d values.

Three replicates of each treatment were used. Two types of control treatments were included: a negative and a positive control (see Table 2). The positive control, containing the radionuclide-spiked groundwater and no sediment, served to account for any radionuclide sorption to labware and filters. The negative control contained sediment and groundwater without the added radionuclides and served to account for background radionuclide activity in the uncontaminated sediment and groundwater and to provide information about radionuclide-detection interferences during analytical analyses. pH and CEC (Rhodes 1986) measurements of each core sample were also measured.

The data were organized according to depth and layers within the Hanford formation. Reidel et al. (1998) observed that the Hanford formation sampled in this borehole had three geologic strata defined by three layers (paleosols). The upper boundary of paleosol horizon 3 occurred at 1.5 m (5 ft), the upper boundary of paleosol horizon 2 at 17.7 m (58 ft), and the upper boundary of paleosol horizon 1 at 49.7 m (163 ft). The complete depths and total thickness of these three contiguous layers are shown in Figure 2 and Table 3 in Reidel et al. (1998). Layer 3 resides between 1.5 and 17.7 m (5 and 58 ft) below ground surface, layer 2 between 17.7 and 49.7 m (58 and 163 ft) below ground surface, and layer 1 between 49.7 and 75.3 m (163 and 247 ft) below ground surface. Reidel et al. reported that the three horizons represent time intervals when soil development took place after three separate Missoula floods. Layer 3, had only 1 sample collected from within; layers 2 and 1 had 10 and 9 samples collected from within, respectively. Thus, a statistical description of layer 3 was not possible because of the lack of replication. Layers 2 and 1 were described using statistics, and a Student's t-test was conducted to evaluate whether the K_d values in each layer differed at the 5% level.

3.0 Results and Discussion

The pH, CEC, and K_d values of the 20 samples are presented in Table 3. pH and CEC measurements were not replicated. The K_d values presented indicate the mean and standard deviation of three replicates. The standard deviations of the K_d values were extremely low, especially for I, Se, Sr, Tc, and U. The low

Table 3. K_d, pH, and Cation-Exchange Capacity Values of Borehole 299-E17-21 Samples[(a)]

Sample ID (B8500--)	Depth		pH	Cation-Exchange Capacity (meq/100 g)	K_d					
	ft	m			Cs (mL/g)	I (mL/g)	Se (mL/g)	Sr (mL/g)	Tc (mL/g)	U (mL/g)
Layer 3[(b)]										
07A	45.9 - 47.9	14.0 - 14.6	8.54	5.07	2,044.8 ± 275.1	0.00 ± 0.01	7.77 ± 0.08	14.09 ± 0.83	-0.01 ± 0.02	0.94 ± 0.12
Layer 2[(b)]										
10A	57.8 - 59.8	17.6 - 18.2	8.80	4.73	2,090.0 ± 305.2	-0.01 ± 0.02	6.80 ± 0.54	14.25 ± 0.49	-0.02 ± 0.03	0.67 ± 0.08
12A	69.4 - 71.0	21.2 - 21.6	8.77	4.60	2,023.8 ± 305.2	0.00 ± 0.03	6.22 ± 0.38	13.81 ± 0.78	0.01 ± 0.00	0.64 ± 0.10
14A	80.3 - 82.8	24.5 - 25.2	8.73	4.62	1,969.8 ± 39.5	-0.03 ± 0.02	6.79 ± 0.32	13.94 ± 0.50	-0.01 ± 0.03	0.67 ± 0.05
15A	90.5 - 93.0	27.6 - 28.3	8.75	4.11	1,502.1 ± 80.1	-0.03 ± 0.03	6.24 ± 0.28	13.64 ± 0.85	0.00 ± 0.02	0.74 ± 0.05
16A	100.5 - 103.0	30.6 - 31.4	8.77	2.32	1,535.9 ± 269.8	0.06 ± 0.17	6.85 ± 0.58	12.81 ± 0.33	-0.01 ± 0.02	0.57 ± 0.04
17A	109.8 - 112.2	33.5 - 34.2	8.52	4.98	2,267.2 ± 388.1	0.00 ± 0.02	8.64 ± 0.38	15.46 ± 0.33	-0.04 ± 0.01	0.68 ± 0.15
19A	121.0 - 123.5	36.9 - 37.6	8.50	4.72	2,861.7 ± 395.7	-0.01 ± 0.01	8.93 ± 0.05	14.25 ± 0.45	-0.02 ± 0.02	0.51 ± 0.08
20A	129.7 - 132.2	39.5 - 40.3	8.52	4.67	2,251.8 ± 291.8	-0.01 ± 0.02	7.55 ± 0.21	15.32 ± 0.37	0.00 ± 0.01	0.65 ± 0.08
21A	141.5 - 144.0	43.1 - 43.9	8.56	4.56	2,072.5 ± 408.9	-0.01 ± 0.01	6.57 ± 0.47	14.91 ± 0.63	0.00 ± 0.02	0.57 ± 0.09
22A	151.9 - 154.4	46.3 - 47.1	8.94	7.33	1,373.9 ± 331.6	0.12 ± 0.04	6.74 ± 0.44	12.18 ± 0.29	0.00 ± 0.02	0.59 ± 0.08
Layer 1[(b)]										
23A	160.4 - 162.9	48.9 - 49.7	8.82	8.41	2,295.2 ± 279.9	0.13 ± 0.06	10.40 ± 0.55	13.04 ± 0.95	-0.01 ± 0.03	0.58 ± 0.05
24A	180.7 - 182.7	55.1 - 55.7	8.81	9.03	2,213.3 ± 454.7	0.02 ± 0.03	6.09 ± 0.24	16.92 ± 0.92	0.00 ± 0.02	0.55 ± 0.05
25A	189.7 - 191.9	57.8 - 58.5	8.89	6.63	1,716.9 ± 484.4	0.09 ± 0.05	5.28 ± 0.09	12.35 ± 0.85	0.01 ± 0.01	0.56 ± 0.07
27A	194.3 - 201.3	59.2 - 61.4	8.88	8.36	1,563.0 ± 259.0	0.06 ± 0.05	4.75 ± 0.44	16.17 ± 1.42	0.00 ± 0.01	0.59 ± 0.08
29A	210.9 - 211.4	64.3 - 64.4	8.84	7.77	2,128.7 ± 423.1	0.23 ± 0.06	5.67 ± 0.24	14.22 ± 0.34	-0.01 ± 0.03	0.50 ± 0.13
31A	214.6 - 1222.6	65.4 - 67.8	8.56	10.98	4,068.2 ± 258.7	0.04 ± 0.07	10.85 ± 0.31	16.90 ± 0.11	-0.03 ± 0.04	0.30 ± 0.12
32A	229.0 - 231.2	69.8 - 70.5	8.93	8.39	1,792.0 ± 315.2	-0.01 ± 0.01	4.40 ± 0.17	16.89 ± 1.72	-0.01 ± 0.01	0.70 ± 0.11
34A	236.1 - 238.1	72.0 - 72.6	8.92	6.21	1,897.0 ± 178.3	0.08 ± 0.08	4.23 ± 0.15	16.92 ± 1.53	-0.02 ± 0.01	0.61 ± 0.16
35A	239.5 - 241.5	73.0 - 73.6	8.89	6.65	1,435.0 ± 133.3	0.01 ± 0.02	3.75 ± 0.17	16.79 ± 2.68	-0.02 ± 0.01	0.68 ± 0.13

(a) Means ± standard deviation; 3 replicates for K_d values; 1 replicate for cation-exchange capacity and pH measurements.

(b) Layers are geologic units within the sandy sequence identified by Reidel et al. (1998). They were identified by three paleosol strata; paleosol horizon 3 at 1.5 m (5 ft), paleosol horizon 2 at 17.7 m (58 ft), and paleosol horizon 1 at 49.7 m (163 ft). These three horizons represent time intervals when soil development took place and are interpreted to be the tops of three separate Missoula floods.

standard deviations are indicative of low variability within the samples and of good experimental technique. Low variability within the sediment sample was accomplished by extensive mixing of the samples prior to taking material from the sample bag (~3 min shaking by hand). The relatively higher variability for Cs K_d values has been observed previously in measurements made in Hanford Site sediments (Parker 1997, Kaplan et al. 1998b). This is likely attributed to the fact that Cs has an extremely high-sorption affinity to 2:1 minerals, such as smectites and illites, and these minerals were not evenly distributed throughout the samples. Ames and Rai (1978) reported Cs K_d values of 4,900 mL/g for smectite and 2,200 mL/g for illite. It is not uncommon for the clay-size fraction to make up only 3% (wt) of the total sediment mass, and for the 2:1 minerals, to make up only 40% of the clay-size fraction. Yet these 2:1 minerals may hold >99% of the Cs sorbed to the sediment. Thus, only a very small difference in the distribution of these strongly sorbing minerals may result in rather larger variability in Cs K_d values.

A statistical description of the data in Table 3 is presented in Table 4. The statistical analyses of the K_d values were conducted using the 20 means presented in Table 3 and not each individual replicate of the 20 means (i.e., there were 20, not 60, observations used in these analyses). The K_d value means for all the samples from the borehole were consistent with previously reported values (as reviewed by Kaplan and Serne 1995). The variance of these K_d values was surprisingly low, suggesting rather uniform distribution throughout the borehole. Some notable exceptions are discussed below. The median did not vary greatly from the mean of each radionuclide K_d value (see Table 4).

The K_d values of Cs, Se, Sr, Tc, and U are consistent with those previously reported and support the conservative K_d values used as input to the ILAW-performance assessment (PA) (Mann et al. 1998): 100, 0, 5, 0, and 0.6 mL/g, respectively. In the case of Cs, Se, and Sr, the data in Table 4 suggest that the ILAW-PA values are very conservative. For Tc and U, the conservative values used in the ILAW-PA are consistent with those reported in Table 4.

Table 4. Statistical Description of the Entire K_d (mL/g) Data Set[(a)]

	pH	Cation-Exchange Capacity (meq/100 g)	K_d					
			Se	I	U	Cs	Sr	Tc
Mean	8.75	6.18	6.73	0.04	0.62	2,055.1	14.74	-0.01
Standard error	0.03	0.50	0.43	0.01	0.03	133.4	0.36	0.00
Median	8.79	5.07	6.66	0.00	0.60	2,034.3	14.25	-0.01
Standard deviation	0.15	2.18	1.90	0.07	0.12	596.5	1.60	0.01
Sample variance	0.024	4.76	3.63	0.00	0.01	355,757	2.57	0.00
Minimum	8.50	2.32	3.75	-0.03	0.30	1,373.9	12.18	-0.04
Maximum	8.96	10.98	10.85	0.23	0.94	4,068.2	16.94	0.01
(a) The statistics analyses were conducted using 20 means for each parameter (n = 20) presented in Table 3.								

Of notable concern are the unusually low I K_d values found for the sediments from borehole 299-E17-21 (see Tables 3 and 4). These findings indicate that the I K_d values may be lower than previously predicted based on a literature review (Kaplan and Serne 1995). The conservative I K_d value used as input for the ILAW-PA was 3.0 mL/g (Mann et al. 1998). This value is appreciably larger than those reported in Table 4. The cause for these unusually low K_d values is not known. Visual inspection of the core samples revealed that they had a coarse texture and that there were relatively fewer fine-textured materials in them. It is concluded that I sorption is strongly dependent on the amount and type of fine-grained minerals in Hanford Site sediments. More recently, Kaplan et al. (1996) measured 12 I K_d values using ILAW-DC sediments. These values ranged from 0.07 to 9.8 mL/g. The mean was 3.85 ± 1.03 mL/g, and the median was 3.65 mL/g. Only two of the measured K_d values in Kaplan et al. (1996) were less than 1 mL/g. Appropriate conservative and best K_d values based on the results from this borehole will be discussed in greater detail in Section 4.0.

The mean pH value, 8.75 ± 0.15, is slightly higher than expected (see Table 4). Generally, the pH of surface sediments and near-surface sediments has been reported to be ~8.0 to 8.4 (Serne et al. 1993; Kaplan et al. 1995, 1996). This slightly higher-than-expected pH value is not likely to have a great impact on K_d values for anions or cations, though it would tend to slightly increase the K_d values of cations (e.g., Cs, Sr) and slightly decrease the K_d values of anions (e.g., I, Se, Tc).

A matrix of simple linear correlation coefficients of the measured parameters is presented in Table 5. Statistically significant correlations are also identified in the table. In general, these correlations do not shed much light on the processes responsible for the sorption of the radionuclides. Many of the significant correlations cannot be explained based on geochemical considerations such as the significant correlations between I K_d and pH, Cs K_d and Se K_d, and Cs K_d and pH. The inverse correlation between pH and Se is well-established and can be attributed to the greater number of anionic adsorption sites in lower-pH systems (Balistrieri and Chao 1990, Fujikawa and Fukui 1997). The negative correlation coefficients between U and both cationic and anionic radionuclides cannot be explained with the data available. The dominant U species in this system were either anionic (as UO_2^{2+} complexes with carbonate and to a lesser extent hydroxyl ligands) or neutral (as UO_2^{2+} complexes with carbonate ligands).

Table 5. Simple Correlation Coefficients for Entire K_d Data Set

K_d	Se	I	U	Cs	Sr	Tc	pH
I	-0.02						
U	-0.30	-0.42					
Cs	0.73[a]	-0.04	-0.57[a]				
Sr	-0.23	-0.26	-0.13	0.30			
Tc	-0.36	0.05	0.13	-0.46[a]	-0.43[a]		
pH	-0.66[a]	0.44[a]	-0.01	-0.60[a]	-0.04	0.31	
CEC	0.09	0.44[a]	-0.49[a]	0.39	0.46[a]	-0.13	0.31

(a) Correlation is significant at the 0.05 level of confidence and 19 degrees of freedom (critical correlation coefficient is 0.43 ($P \leq 0.05$; d.f. = 19).

Cation-exchange capacity is a measure of the total number of cationic exchange sites on the solid phase. Thus, the radionuclides that sorb to sediments primarily via cation-exchange reactions would be expected to be correlated to this parameter. For the borehole 299-E17-21 samples, the CEC was significantly correlated to I, Sr, and U K_d values (see Table 5). Because I and U are primarily anionic (I^- and $UO_2[CO_3]^{2-}$) under the conditions of these tests, a negative correlation between CEC and I and U K_d values was expected. Instead, a positive correlation was found with the I and a negative correlation was found with the U. The significant correlation between CEC and Sr reinforces the generally belief that Sr adsorption is almost exclusively controlled by cation-exchange reactions.

Statistical analyses were also conducted to evaluate whether the geologic layers identified by Reidel et al. (1998) had unique K_d values. Unfortunately, only one core sample was collected from layer 3, whereas layers 2 and 1 had 10 and 9 core samples, respectively. Thus, statistics could not be applied to layer 3. A significant difference (P value ≤ 0.05) was identified between the pH, CEC, I K_d, and Sr K_d means of layers 2 and 1. The likely explanation for the differences in I and Sr K_d values may be attributed to the fact that the pH and the CEC values in layer 1 are slightly greater than those in layer 2. As shown in Table 5, I and Sr K_d values are significantly correlated to CEC. Thus, it appears quite likely that the resulting differences between these two layers may be attributed to the corresponding significant differences in the CEC values of the two layers. With regard to pH, a common trend in geochemistry is that, as pH increases, K_d values of anions tend to decrease and the K_d values of cations tend to increase. There was no significant difference between the Cs, Se, Tc, and U K_d values for layer 2 versus layer 1. Some additional results from the statistical analyses of these data are presented in the Appendix.

Qualitatively, not statistically, comparing the single measurements of layer 3 with the means of layers 2 and 1 reveals some interesting trends. The pH values tended to decrease with depth. The cause of this is not known but may be attributed to higher CO_2 concentrations commonly found in lower geologic strata (Wood and Petraitis 1984). The other trend that can be seen in Table 6 is that the K_d values in layer 3 are generally more similar to those in layer 2 than to those in layer 1, except Cs.

Table 6. Average K_d Values Measured in Sediments Collected from Borehole 299-E17-21[(a)]

Formation	pH	Cation-Exchange Capacity (meq/100)	K_d					
			Cs (mL/g)	I (mL/g)	Se (mL/g)	Sr (mL/g)	Tc (mL/g)	U (mL/g)
Layer 3	8.54	5.07	2044.8	0.00	7.77	14.09	-0.01	0.94
Layer 2	8.69 ± 0.15	4.66 ± 1.57	1994.9 ± 441.2	0.01 ± 0.05	7.13 ± 0.95	14.05 ± 1.04	-0.01 ± 0.00	0.63 ± 0.07
Layer 1	8.84 ± 0.11	8.00 ± 1.57	2123.2 ± 793	0.08 ± 0.07	6.17 ± 2.64	15.57 ± 1.93	-0.01 ± 0.01	0.56 ± 0.11
P value[(b)]	0.02	1E-5	0.66	0.03	0.29	0.04	0.68	0.15

(a) The data used to generate the statistics in this table are presented in Table 3. Layer 3 had 1 observation; layer 2 had 10 observations; layer 1 had 9 observations.

(b) The P value is the probability that the pH, CEC, and K_d values in layers 2 and 1 are different. For the purposes of this study, a P value greater than 0.05, 5% probability, indicated that the means for each layer are not significantly different.

4.0 Conclusions

The K_d values of Cs, I, Se, Sr, Tc, and U were measured in 20 sediments collected from borehole 299-E17-21. Additionally, the pH and the CEC of these sediment samples were measured. Statistical analyses using Student's t-test and correlation were conducted with the measured values.

Two tables were generated to summarize these data. Table 7 provides the conservative and best estimates of K_d values, assuming that the Hanford formation will be divided into the three geologic layers identified. Table 8 provides the conservative and best estimates of K_d values, assuming that the Hanford formation will be treated as a single modeling unit. Which of these two tables, or more specifically, which of these two conceptual models, that will ultimately be used in the performance assessment will depend on these data as well as the characterization data generated by Reidel et al. (1998) and the Fayer et al. letter report, as well as future calculations to be conducted in fiscal year 1999. Presumably, if significant differences in other parameter values such as hydraulic conductivity are observed between the layers, then it may be decided that introducing the added complexity of three layers may be warranted. Otherwise, the most conservative estimate of the combined layers will need to be used for the ILAW-PA.

The best estimate for each constituent's K_d value was the calculated median value, and the uncertainty was chosen as the standard deviation. The median was selected, as opposed to the mean, so as not to have outliers or extreme values overly influence the best estimate. The conservative estimate was based on the minimum value, except for the U K_d estimate. The conservative U K_d estimate was based on the second-to-lowest value (0.5 mL/g) because of the presence of an unusually low value (0.3 mL/g) that was not consistent with other values measured from this borehole or previously reported values (Kaplan and Serne 1995). For the radionuclide K_d values for which there were no significant differences between the means of layers 2 and 1 (i.e., for Cs, Se, Tc, and U), the same K_d estimates were used in all three

Table 7. Conservative and Best Estimates of K_d Values of Layers 1, 2, and 3[(a)]

Radionuclide	Layers 3 and 2 K_d (mL/g)		Layer 1 K_d (mL/g)	
	Conservative	Best	Conservative	Best
Cs	1,370	2,050 ± 440	1,370	2,050 ± 440
I	0	0 ± 0	0	0.1 ± 0.1
Se	3.8	6.7 ± 1.9	3.8	6.7 ± 1.9
Sr	12.0	14.3 ± 1.6	12.0	16.5 ± 1.9
Tc	0.0	0 ± 0	0.0	0 ± 0
U	0.5	0.6 ± 0.1	0.5	0.6 ± 0.1

(a) Different K_d values were assigned to each layer when statistical analyses determined that they differed at the 5% level of confidence (see Table 6). Otherwise, the same K_d values were assigned for all three layers. Conservative estimates were based on the minimum value (see Table 3, except U) and the best estimates were based on the median ± standard deviation (see Table 4 and the Appendix).

Table 8. Conservative and Best Estimates of K_d Values for the Hanford Formation

Radionuclide	Conservative K_d Value[(a)] (mL/g)	Best K_d Value[(b)] (mL/g)
Cs	1,370	2,030 ± 597
I	0	0 ± 0
Se	3.8	6.7 ± 1.9
Sr	12.0	14.3 ± 1.6
Tc	0.0	0 ± 0
U	0.5	0.6 ± 0.1

(a) Conservative K_d value estimates are based on the lowest value for each radionuclide presented in Table 3 (except U, which used the second-lowest measured K_d value; see explanation in text).
(b) Best K_d value estimates are the median ± standard deviation from the 20 sediments presented in Table 3.

layers (see Table 6). Because there was only one sample from layer 3, K_d estimates for this layer were assigned the same values as those in layer 2. This is likely a conservative estimate of layer 3 K_d values because they tended to be the same or greater than those of layer 2 (see Table 6).

Based on the K_d values presented in Table 7, the added "credit" (higher K_d values) and accuracy gained for the ILAW-PA are not offset by the added complexity introduced by increasing the number of K_d regions from one to three. For example, if the multilayer conceptual model is used, the I K_d in layer 1 is increased only slightly to 0.1 mL/g, compared to when the entire Hanford formation is assigned a single K_d value of 0 mL/g. Further, the Sr K_d is already high and, therefore, little is gained in accuracy or "credit" by increasing the Sr K_d value of layer 1 from 14.3 to 16.5 mL/g. Consequently, the best set of K_d values to use, based on this data set alone, are those presented in Table 8.

Overall, the estimates appearing in this table are consistent with values used for the ILAW-PA, with some notable exceptions. The conservative K_d estimates used were 100 mL/g for Cs, 3 mL/g for I, 0 mL/g for Se, 5 mL/g for Sr, 0 mL/g for Tc, and 0.6 mL/g for U. The conservative K_d estimates for Tc and U reported in Tables 7 and 8 are approximately the same as those used for the interim PA. The conservative values for Cs, Se, and Sr used in the interim PA were appreciably more conservative than necessary. The conservative I K_d value in this new work is appreciably less than that used in the interim PA (3 mL/g). The I K_d estimate used in the interim PA was based on a literature review of K_d values measured using Hanford Site sediments, which revealed that the range of I K_d values was 0.7 to 15 mL/g with an average of 3.1 mL/g (Kaplan and Serne 1995). The cause for the lower I K_d values is not known, though the sediments used in this study clearly had appreciably lower concentrations of fine materials than the Hanford Site sediments previously used in I sorption measurements. These differences in K_d values underscore the importance of basing K_d estimates for the ILAW-PA on measurements using site-specific sediments.

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Appendix

Additional Statistics

Appendix

Additional Statistics

Table A.1. Descriptive Statistics of the K_d Values in Layers 1 and 2

Layer	K_d						Cation-Exchange Capacity
	Se	I	U	Cs	Sr	Tc	
Statistics for Layer 1							
Mean	6.47	0.08	0.55	2,209.3	15.43	-0.01	8.00
Standard error	0.93	0.03	0.04	280.3	0.68	0.01	0.55
Median	5.47	0.07	0.57	2,012.8	16.53	-0.01	8.06
Standard deviation	2.64	0.07	0.11	792.9	1.93	0.01	1.57
Sample variance	6.96	0.01	0.01	628,731.2	3.72	0.00	2.45
Minimum	4.23	-0.01	0.30	1,563.0	12.35	-0.03	6.21
Maximum	10.85	0.23	0.70	4,068.2	16.94	0.01	10.98
Statistics for Layer 2							
Mean	7.13	0.01	0.63	1,994.88	14.06	-0.01	4.66
Standard error	0.30	0.01	0.02	139.33	0.33	0.00	0.42
Median	6.79	-0.01	0.64	2,048.15	14.09	0.00	4.62
Standard deviation	0.95	0.05	0.07	440.6	1.04	0.01	1.27
Sample variance	0.90	0.00	0.00	194,133.3	1.08	0.00	1.63
Minimum	6.22	-0.03	0.51	1,373.9	12.18	-0.04	2.32
Maximum	8.93	0.12	0.74	2,861.7	15.46	0.01	7.33

Table A.2. Analysis of Variance Tables Comparing the K_d Means in Layer 1 Versus in Layer 2

Selenium K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	71.32488	7.132488	0.897275
Layer 1	9	55.49897	6.166552	6.907754

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	4.419629	1	4.419629	1.186243	0.291288	4.451323
Within groups	63.33751	17	3.725736			
Total	67.75714	18				

Iodide K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	0.070373	0.007037	0.00212
Layer 1	9	0.646212	0.071801	0.005382

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	0.019868	1	0.019868	5.435528	0.032292	4.451323
Within groups	0.062139	17	0.003655			
Total	0.082007	18				

Table A.2. (contd)

Uranium K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	6.286995	0.6287	0.004678
Layer 1	9	5.077822	0.564202	0.013306

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	0.019705	1	0.019705	2.255022	0.151528	4.451323
Within groups	0.148548	17	0.008738			
Total	0.168253	18				

Cesium K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	19948.76	1994.876	194133.3
Layer 1	9	19109.23	2123.247	616752.4

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	78059.18	1	78059.18	0.198617	0.661463	4.451323
Within groups	6681219	17	393012.9			
Total	6759279	18				

Table A.2. (contd)

Strontium K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	140.5663	14.05663	1.076624
Layer 1	9	140.2091	15.57878	3.456325

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	10.97506	1	10.97506	4.996649	0.039103	4.451323
Within groups	37.34021	17	2.196483			
Total	48.31527	18				

Technetium K_d: Layer 1 vs. 2

ANOVA: Single Factor

Groups	Count	Sum	Average	Variance
Layer 2	10	-0.08563	-0.00856	0.000182
Layer 1	9	-0.10087	-0.01121	0.000193

ANOVA

Source of Variation	SS	df	MS	F	P-value	F crit
Between groups	3.31E-05	1	3.31E-05	0.177105	0.679146	4.451323
Within groups	0.00318	17	0.000187			
Total	0.003213	18				

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