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Distribution and Range of Radionuclide Sorption Coefficients in a Savannah River Site Subsurface: Stochastic Modeling Considerations – 10259

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ABSTRACT

The uncertainty associated with the sorption coefficient, or K_d value, is one of the key uncertainties in estimating risk associated with burying low-level nuclear waste in the subsurface. The objective of this study was to measure >648 K_d values and provide a measure of the range and distribution (normal or log-normal) of radionuclide K_d values appropriate for the E-Area disposal site, within the Savannah River Site, near Aiken South Carolina. The 95% confidence level for the mean K_d was twice the mean in the Aquifer Zone (18–30.5 m depth), equal to the mean for the Upper Vadose Zone (3.3 – 10 m depth), and half the mean for the Lower Vadose Zone (3.3 – 18 m depth). The distribution of K_d values was log normal in the Upper Vadose Zone and Aquifer Zone, and normal in the Lower Vadose Zone.

To our knowledge, this is the first report of natural radionuclide K_d variability in the literature. Using ranges and distribution coefficients that are specific to the hydrostratigraphic unit improved model accuracy and reduced model uncertainty. Unfortunately, extension of these conclusions to other sites is likely not appropriate given that each site has its own sources of hydrogeological variability. However, this study provides one of the first examples of the development stochastic ranges and distributions of K_d values for a hydrological unit for stochastic modeling.

INTRODUCTION

An important aspect of contemporary risk assessment is consideration of the variability of risk assessment parameters spatially, temporally, or across populations. Due to their variability, parameters are often more appropriately characterized by distributions rather than by single values. Risk is often quantified discretely; either by a probability for stochastic effects or by a hazard index for deterministic effects. However, due to the inherent variability of risk assessment parameters and uncertainties, risk is more appropriately characterized by a distribution. The distribution of risk due to parameter variability is calculated by propagating parameter distributions through the contaminant release, transport, exposure, and consequence assessment steps of the risk calculation process. This is typically accomplished using Monte Carlo methods, and the process is sometimes referred to as stochastic modeling. Specification of parameter distributions is thus a critical aspect of stochastic modeling. These parameters may include a mean, range, and distribution shape (e.g., normal or log-normal).

The primary means utilized for Low-Level Radioactive Waste disposal at the Savannah River Site's E-Area is shallow-land burial. The burial grounds include low-activity waste vaults, intermediate-level vaults, engineered trenches, slit trenches, and components-in-grout trenches.

These vaults and trenches are used to store many different types of Low Level Radioactive Waste including paper, plastics, wood, cloth, spent ion exchange resins, metal, concrete debris, and glass.

As part of its regulatory compliance program, the Savannah River Site must perform risk analyses, or performance assessments, of its Low-Level Radioactive Waste disposal activities at E-Area. Given the variety of different soil layers that are present at different depths below the surface of the E-Area burial grounds, the degree to which any given radionuclide sorbs within the system as a whole is largely unknown. Without the benefit of site-specific data, risk analyses and performance assessments regarding sub-surface radionuclide contaminants can be uncertain undertakings. With that in mind, one of the most important risk assessment parameters for contaminant transport from these buried wastes is the sediment-water distribution coefficient, K_d, for the sediments in immediate contact with the radionuclide in groundwater. This K_d is defined as the equilibrium concentration of a radionuclide in the solid phase divided by the concentration of the radionuclide in the aqueous phase. The value of this coefficient allows for estimation of the contaminant velocity relative to the ground water velocity (known as the retardation factor) and thus allows for calculation of contaminant travel time to a point of compliance.

Modeling of the type used in risk assessment is subject to two types of uncertainty in the parameters that are used to quantify the various physical, chemical, or biological processes that are being modeled. These are aleatory uncertainty and epistemic uncertainty. Aleatory uncertainty is related to chance, and it refers to the variability of parameters that occur over time, space or across a population [1]. Epistemic uncertainty is related to limitations of knowledge. These limitations may include uncertainty related to the completeness of a model, uncertainty in the distributions associated with parameter variability, and a lack of available data. Whereas an aleatory uncertainty analysis yields a risk distribution, an epistemic uncertainty analysis yields confidence limits on that distribution. Aleatory uncertainty (i.e., variability) is determined by propagating parameter distributions through a risk assessment model. This is usually accomplished using standard Monte Carlo techniques. The determination of epistemic uncertainty is a much more complex problem. Monte Carlo techniques can be combined with expert judgment to evaluate the epistemic uncertainty in variability distributions, but methods have not been established for evaluating epistemic uncertainty in models.

Aleatory uncertainty of a parameter requires measurement data, either from the laboratory or the field. The distribution of these data can be expressed in tabular form, can be empirically fit, or can be approximated by theoretical distributions. Theoretical distributions often used for approximating risk assessment parameters are uniform, normal, log-normal, and beta. Bayesian updating may also be used with regional or generic distributions as the prior [2]. Finally, a combination of methods may be used for parameter distribution determination [3].

The objective of this research was to evaluate the range and distribution of K_d values in E-Area on the Savannah River Site. The approach taken was to measure radionuclide K_d values for 27 sediment samples collected from E-Area and to assess the K_d value range and distribution characteristics. The specific objectives of this research were as follows:

1. to measure distribution coefficients for Am-241, Cd-109, Ce-139, Co-57, Co-60, Cs-137, Hg-203, Sr-85, and Y-88 in E-Area Savannah River Site sediments;
2. to characterize the distribution of these K_d values in the E-Area sediments (normal or log-normal); and

3. to make practical recommendations for distributions and ranges of K_d values for stochastic modeling of K_d values not measured in this study.

Additionally, basic sediment characterization (described below) was conducted and the results were correlated to K_d values.

MATERIALS AND METHODS

A detailed description of the materials and methods are presented in Grogan et al. [4]. Following is a brief description, sufficient to permit understanding the results. Field sediment sampling was conducted by Savannah River National Laboratory personnel. K_d measurements and sediment characterization was conducted by Clemson University personnel. X-ray Diffraction (XRD) analyses and Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) was conducted by University of Georgia personnel. Statistical analyses were conducted by Savannah River National Laboratory and Clemson University personnel.

Sediment samples were collected from a single borehole (BGO-3A) located in an uncontaminated portion of E-Area. The 27 depth-discrete samples were collected from depths ranging from 3.3 m to 30.5 m below ground surface (Figure 1). K_d values of eight radionuclides were determined in triplicate of the 27 sediment samples by measuring the radionuclide concentration in the aqueous and solid phases. Additionally, several dozen positive and negative control samples were included in these experiments. Several sediment properties were also measured to determine if correlations could be made between the K_d values and sediment properties. The sediment properties measured were pH, total Fe/Al/Ti (as measured by X-ray fluorescence; XRF), dithionite extractable Fe/Al/Ti (the approximate Fe, Al, and Ti concentrations in the oxyhydroxide coatings of sediment particles), clay content, and cation exchange capacity.

For data analysis, cumulative distribution graphs of the K_d data were constructed for each radionuclide for the whole core and for each of the three subsurface strata: the Upper Vadose Zone, the Lower Vadose Zone, and the Aquifer Zone. These data were displayed in the form of probability and log-probability plots, which linearize normal and log-normal distributions, respectively. This permitted visual identification of the distributions which might be approximated as either normal or log-normal. Skewness and kurtosis were also determined for each distribution. A positive kurtosis indicated a curve with a longer tail than normal whereas a negative kurtosis indicated a curve that was flatter than normal. A positive skewness indicated tailing of the curve to the right whereas a negative skewness indicated tailing of the curve to the left.

Simple and multiple regression analyses were conducted between the various K_d values and the sediment characterization parameters. Again, additional details of the statistical methods used in the study are described in Grogan et al. [4].

RESULTS

The results of the batch sorption tests for the BGO-3A core are displayed in Figure 2. K_d values in the figure represent the median value measured for the three trials at each core depth. Values ranged from less than 1 mL/g for ^{85}Sr to greater than 1000 mL/g for ^{88}Y and ^{139}Ce. Also, there was considerable variability in the K_d values for any given radionuclide. For example, K_d values for ^{57}Co and ^{60}Co ranged from approximately 10 mL/g to over 1000 mL/g, suggesting a strong dependence of K_d on sediment properties. Factors such as mineral content, cation exchange capacity, and pH are known to have a significant effect on the observed K_d for a given element. Error bars have been omitted from Figure 2 due to the large uncertainties that were observed for the small sample size examined (three trials) for a given sample depth. However, it is believed that the observed trends are valid because of the similar corresponding fluctuations that were observed for many of the isotopes. For example, ^{57}Co and ^{60}Co display almost identical mean K_d values throughout the depth profile. Similar trends were noted for mercury, cadmium, and cesium as well.

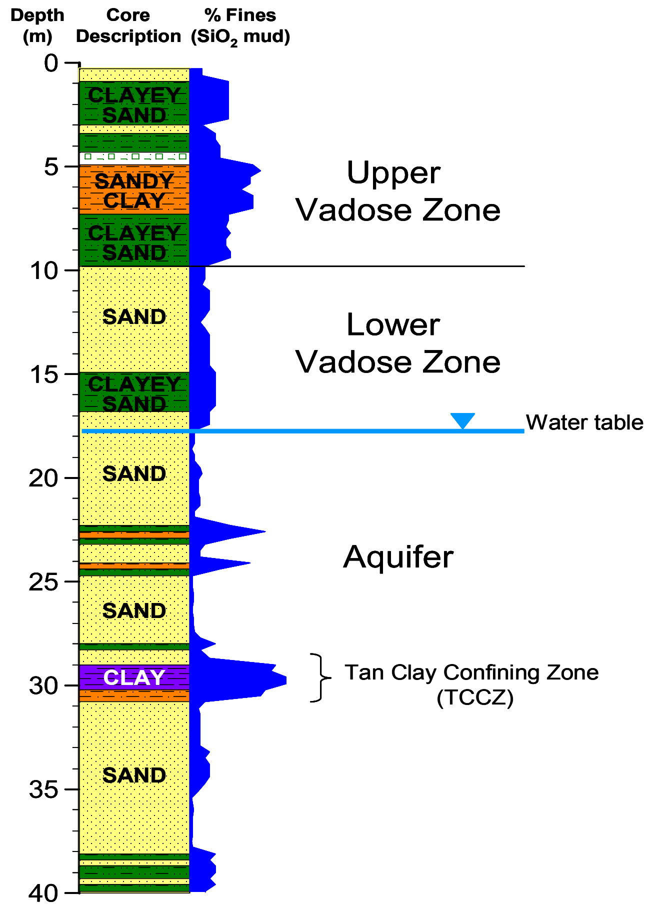

Figure 1. sub-surface profile of the BGO-3A core from the D-Area of Savannah River Site, Aiken, SC.

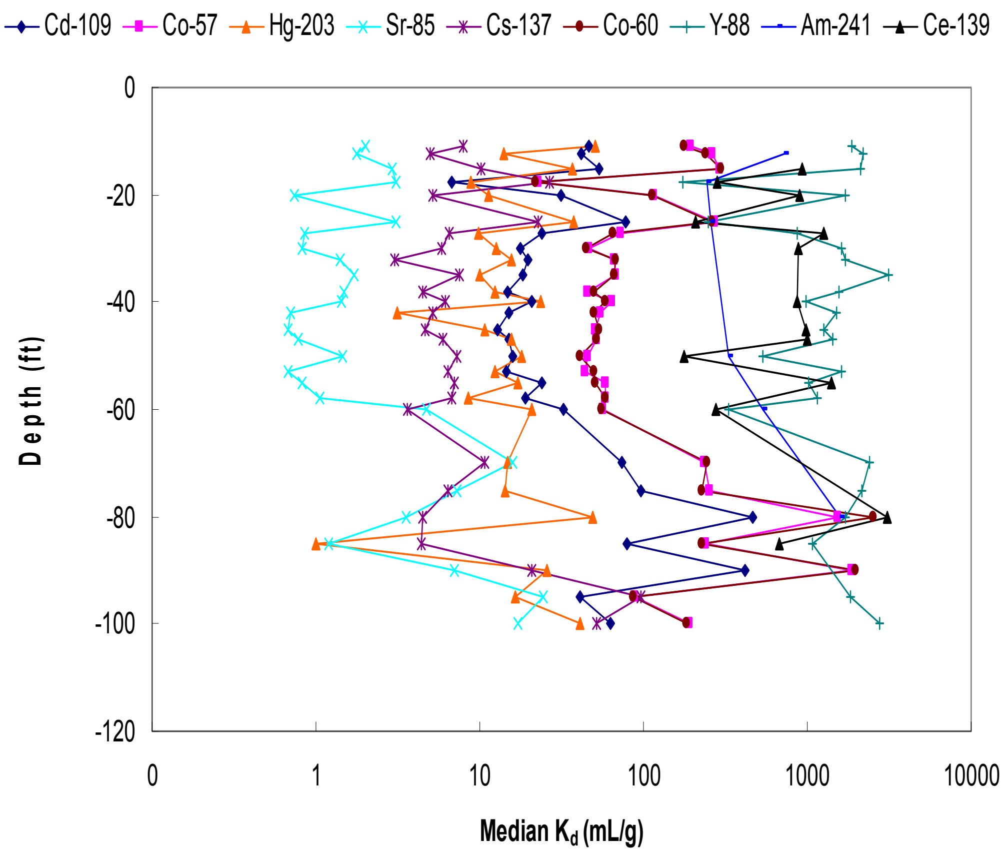

Figure 2. Sub-surface profiles of distribution coefficients of radionuclides for the BGO-3A core from the E-Area burial grounds of SRS

Summary statistics of the data are presented in Table 2. The mean for each radionuclide represents the average of 27 values, one mean for each depth from the BGO-3A core. These values, in turn, are the average for three samples. Values for ^{241}Am and ^{139}Ce are omitted because of the relatively small amount of data that could be collected for each of these isotopes due to their extremely low aqueous concentrations (most of the added radionuclides were adsorbed by the sediment). The mean K_d values for these sediments represent the lower quartile of their expected range based on a literature review [5, 6, 7]. Also of note, in some cases the mean K_d value was more than a factor of four greater than the median K_d value for a given sample depth. This observation indicates that some of the mean K_d values presented in Table 2 have likely been skewed by a few very large values. The median K_d values of the radionuclides were ranked as follows:

Y-88 >> Co-57,60 > Cd-109 > Hg-203 > Cs-137 >> Sr-85.

Americium and cerium have not been included in this ranking because of the inability to generate enough data for sufficient statistical power.

Table 2. Compilation of summary statistics for radionuclides K_d values.

	Radionuclide K_d (mL/g)						
Sample Statistic	^{109}Cd	^{137}Cs	^{57}Co	^{60}Co	^{203}Hg	^{85}Sr	^{88}Y
Mean	89	13	252	306	21	4.0	1641
Std. Error	36	3.8	84	117	3.2	1.07	139
Median	30	6.6	70	72	14	1.83	1573
Std. Deviation	185	20	436	610	17	5.6	709
Minimum	9.1	3.5	34	33	2.1	0.21	295
Maximum	927	97	1869	2710	71	23	3134

Correlations Between K_d Values and Soil Properties

Simple correlation coefficients were calculated between the K_d values and the soil parameters for all the sediment zones and for the three stratified sub-surface zones (Table 3). Examination of Table 3 reveals that the correlation coefficients are not necessarily consistent when comparing the whole core correlations to the stratified correlations. Most notably, some of the expected K_d correlations with soil characteristics become more apparent in the stratified data. For example, greater positive correlations between the Cs-137 K_d values and clay content were noted in the stratified sub-surface data than when the whole data set was placed together. Also, the expected increased levels of positive correlation were noted for the K_d values of Co with sediment pH. These correlations were less significant for the core as a whole.

Table 3. Correlation analysis for K_d and sediment characterization parameters

Isotope	Soil Parameter	Whole Core	Upper Vadose Zone	Lower Vadose Zone	Aquifer Zone
^{109}Cd	CEC (meq/100g)	0.04	0.33	0.21	-0.16
	Soil pH	0.27	0.70	0.55	0.15
	Avg. Clay (%)	-0.21	-0.21	0.18	-0.18
	Al Content (ppm)	0.56	0.34	-0.04	0.60
	Ti Content (ppm)	0.83	0.63	-0.03	0.81
	Mn Content (ppm)	0.08	0.72	-0.06	0.28
	Fe Content (ppm)	0.65	0.61	0.34	0.84
^{137}Cs	CEC (meq/100g)	0.97	0.91	0.63	0.98
	Soil pH	-0.22	0.26	-0.22	-0.48
	Avg. Clay (%)	0.35	0.78	0.78	0.90
	Al Content (ppm)	0.62	0.95	-0.01	0.58
	Ti Content (ppm)	0.01	0.28	-0.41	-0.20
	Mn Content (ppm)	0.21	0.55	-0.20	0.77
	Fe Content (ppm)	0.36	0.80	-0.30	0.22
^{57,60}Co	CEC (meq/100g)	0.01	0.29	-0.31	-0.16
	Soil pH	0.28	0.70	0.88	0.19
	Avg. Clay (%)	-0.18	-0.10	-0.17	-0.17
	Al Content (ppm)	0.54	0.23	0.24	0.58
	Ti Content (ppm)	0.82	0.35	0.06	0.81
	Mn Content (ppm)	0.06	0.43	0.01	0.27
	Fe Content (ppm)	0.63	0.38	0.45	0.83
^{203}Hg	CEC (meq/100g)	0.30	0.36	0.71	0.24
	Soil pH	0.27	0.56	0.00	0.06
	Avg. Clay (%)	0.15	-0.03	0.51	0.12
	Al Content (ppm)	0.34	0.29	-0.10	0.30
	Ti Content (ppm)	0.31	0.66	0.21	0.30
	Mn Content (ppm)	0.29	0.36	-0.69	0.12
	Fe Content (ppm)	0.43	0.37	0.11	0.35
^{85}Sr	CEC (meq/100g)	0.83	0.95	0.05	0.85
	Soil pH	-0.21	0.59	0.47	-0.60
	Avg. Clay (%)	0.08	0.75	-0.03	0.77
	Al Content (ppm)	0.50	0.89	0.52	0.45
	Ti Content (ppm)	0.10	0.26	0.31	-0.25
	Mn Content (ppm)	0.06	0.45	-0.17	0.58
	Fe Content (ppm)	0.25	0.70	0.69	0.10
^{88}Y	CEC (meq/100g)	0.19	-0.55	-0.49	0.50
	Soil pH	-0.25	0.03	0.52	-0.72
	Avg. Clay (%)	-0.17	-0.46	-0.18	0.42
	Al Content (ppm)	0.00	-0.71	0.59	0.37
	Ti Content (ppm)	0.00	-0.32	0.07	0.01
	Mn Content (ppm)	-0.33	-0.55	0.16	0.17
	Fe Content (ppm)	-0.26	-0.66	0.46	0.21

Distribution of K_d Values

Log-probability plots of the whole core distributions are presented in Figure 3. Based on visual examination, the distributions for ^{109}Cd, ^{57}Co, ^{60}Co, ^{203}Hg, ^{85}Sr, ^{137}Cs, and ^{88}Y show relatively minor departures from linearity and could reasonably be described as log-normal. There were insufficient data for ^{241}Am and ^{139}Ce to make a judgment about the validity of a log-normal approximation. None of the plots are linear, indicating that the distributions can not be described as normal.

The results of the visual and Shapiro-Wilk statistical tests for normality (or log-normality) are presented in Table 4. The test statistics (W) for each radionuclide along with their associated p-values are listed in the table. The p-values indicate the confidence level at which the null hypothesis that the K_d values are normally (or log-normally) distributed can be rejected. For example, a p-value of 0.05 indicates that the null hypothesis can be rejected at the 95% confidence level. Based on the results of these tests, none of the isotopes could be approximated by normal or log-normal distributions except for Hg-203 which indicated log-normal distribution characteristics. However, it should be noted that the Shapiro-Wilk test is sensitive to even small deviations from normality, thus limiting its practical value in the context of scientific applications [8]. In Table 4, if the sub-surface K_d values could not be characterized as either normally or log-normally distributed based on the Shapiro-Wilk test or based on visual inspection, then "Neither" is listed for the K_d characterization.

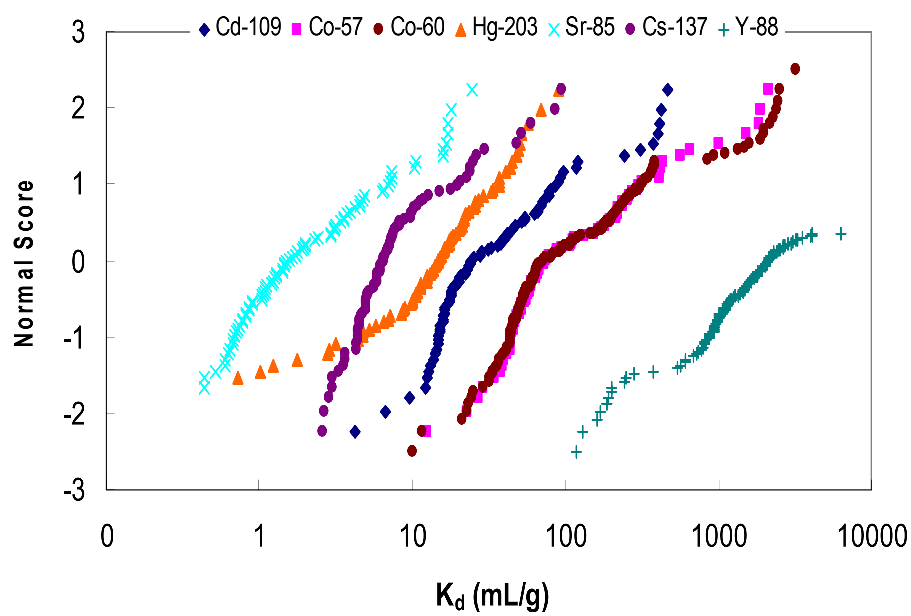

Figure 3. Log-probability plots of the whole core distribution of Cd-109, Co-57, Co-60, Hg-203, Sr-85, Cs-137 and Y-88 K_d values. Except for Y-88, these K_d values can be approximated as having log-normal distributions.

Distributions like those generated for the core as a whole were also developed for each of the sub-surface strata. These probability and log-probability plots can be viewed in Figure 5. Shapiro-Wilk tests were also completed for the stratified distributions. A summary of these results is listed in Table 4.

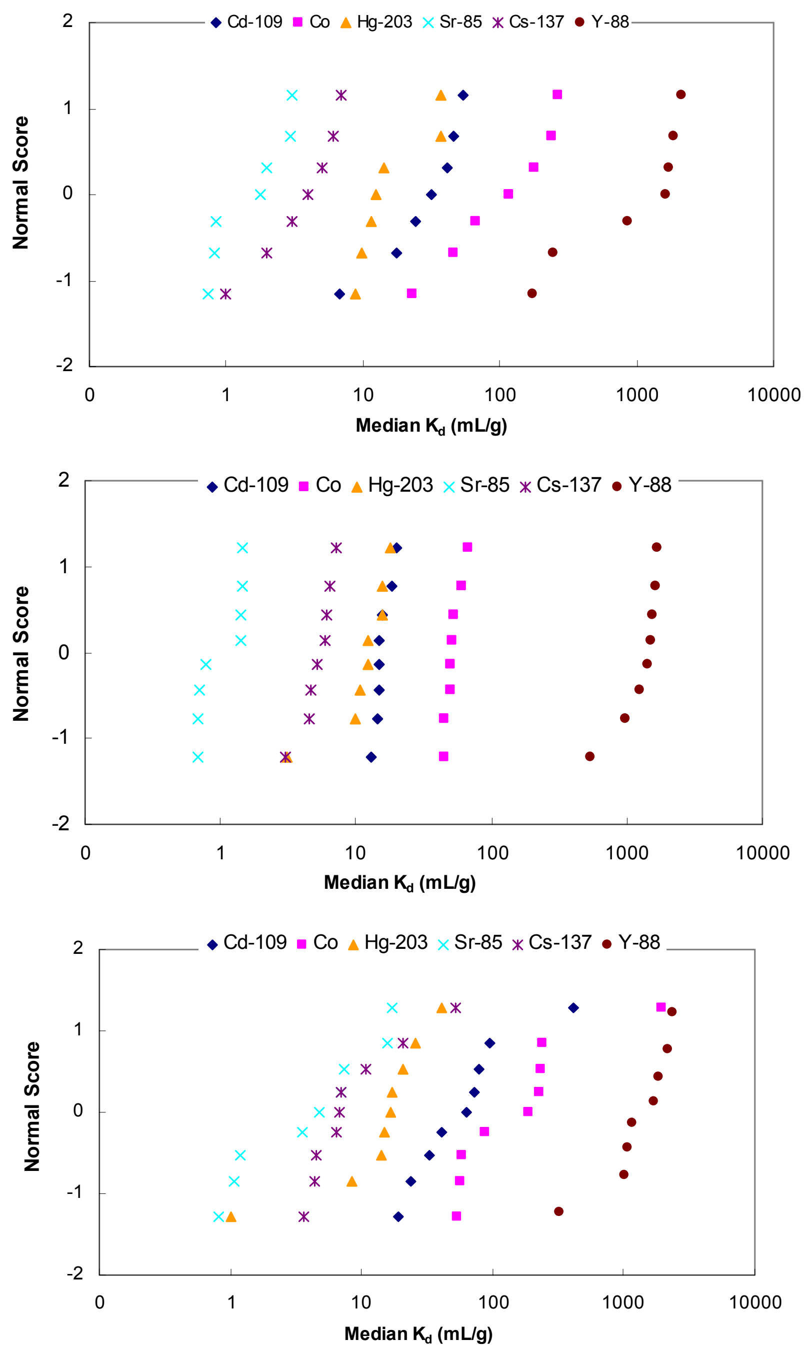

Figure 5. Log-probability plots of K_d values in the (top plot) Upper Vadose, (middle plot) Lower Vadose, and (lower plot) Aquifer Zones.

Based on visual inspection, in the Upper Vadose Zone, Cd-109, Co-57, Co-60, and Y-88, the isotopes with the highest relative K_d values of the radionuclides included, displayed an apparent normal distribution while Sr-85 could be approximated by a log-normal distribution. Cesium and mercury could not be approximated by either distribution type. Examining the Lower Vadose Zone, the K_d values for all of the isotopes could be approximated by a normal distribution. Finally, in the Aquifer Zone, Y-88 displayed apparent normal distribution characteristics for K_d while Cd-109 and Sr-85 could be approximated with a log-normal distribution. The remaining isotopes, Hg-203, Cs-137, and Co57, and Co-60, deviated greatly from linearity in both the probability and log-probability plots and, thus, could not be characterized by either distribution.

The results of the Shapiro-Wilk tests confirm many of the visual approximations described above. However, there were a few cases of disagreement between the visual approximation and the statistical test. These differences can be attributed to the subjective nature of the visual approximation and to the relatively high sensitivity of the Shapiro-Wilk test to only small deviations from normality.

Table 4. Summary of stratified K_d value distributions for the Upper Vadose, Lower Vadose, and Aquifer Zones

		Normal		Log-Normal		Shapiro-Wilk	Visual
Isotope	Strata[1]	W^2	p-value	W^2	p-value	K_d Distribution	K_d Distribution
^{109}Cd	UVZ	0.98	0.9536	0.94	0.5930	Normal	Normal
	LVZ	0.88	0.1446	0.94	0.6147	Log-Normal	Normal
	AZ	0.69	0.0010	0.91	0.2858	Log-Normal	Log-Normal
^{137}Cs	UVZ	0.75	0.0075	0.84	0.0729	Neither	Neither
	LVZ	0.89	0.1954	0.9	0.3473	Normal/Log-Normal	Normal
	AZ	0.64	0.0003	0.86	0.1067	Neither	Neither
$^{57,60}Co$	UVZ	0.91	0.3810	0.91	0.3407	Normal/Log-Normal	Normal
	LVZ	0.90	0.2565	0.93	0.5361	Normal/Log-Normal	Normal
	AZ	0.63	0.0002	0.84	0.0626	Neither	Neither
^{203}Hg	UVZ	0.8	0.0267	0.84	0.0838	Neither	Neither
	LVZ	0.97	0.8659	0.85	0.1174	Normal	Normal
	AZ	0.93	0.5153	0.83	0.0472	Normal	Neither
^{85}Sr	UVZ	0.84	0.0766	0.83	0.0638	Neither	Log-Normal
	LVZ	0.80	0.0220	0.78	0.0128	Neither	Normal
	AZ	0.85	0.0665	0.92	0.3790	Log-Normal	Log-Normal
^{88}Y	UVZ	0.86	0.1240	0.77	0.0148	Neither	Normal
	LVZ	0.86	0.0893	0.64	0.0009	Neither	Normal
	AZ	0.96	0.7918	0.78	0.0127	Normal	Normal

[1] UVZ = Upper Vadose Zone; LVZ = Lower Vadose Zone; AZ = Aquifer Zone.
[2] W = the Shapiro-Wilk statistic and the p-value to the right is the associated probability associated with it.

CONCLUSIONS AND RECOMMENDATIONS

Based on K_d measurements made on 27 sediment samples collected from the E-Area of the Savannah River Site of eight isotopes and three replicates (648 total Kd measurements) some general rules have been established for assigning 95-percentile range and type of distributions for the other 55 radionuclide K_d values of interest to the Savannah River Site performance assessment. These general rules are based not only on these measurements, but also on geochemical/geological considerations, and parsimony.

- The 95% confidence level for the mean K_d was twice the mean in the Aquifer Zone, equal to the mean for the Upper Vadose Zone, and half the mean for the Lower Vadose Zone.
- The distribution of K_d values was log normal in the Upper Vadose Zone and Aquifer Zone, and normal in the Lower Vadose Zone.

To our knowledge, this is the first report of radionuclide K_d variability in the literature. This data supports the assignment of unique ranges and distributions of radionuclide K_d values by hydrostratigraphic unit. Perhaps more importantly, it supports the use of more narrow ranges of K_d values (0.5x, 1x, & 2x the mean) compared to using the distributions measured in the entire subsurface region of interest (one to two orders of magnitude of the mean). Using ranges and distribution coefficients that are specific to the hydrostratigraphic unit will improve model accuracy and reduces model uncertainty. Unfortunately, extension of these conclusions to other sites is likely not appropriate given that each study site has its own source of hydrogeological variability. However, this study does provide one of the first examples of developing a stochastic range and distribution of K_d values for stochastic modeling.

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