RANGE AND DISTRIBUTION OF TECHNETIUM K$_d$ VALUES IN THE SRS SUBSURFACE ENVIRONMENT

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October 28, 2008

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CEC	Cation exchange capacity
DCB	Dithionite citrate buffer
K_d	Distribution coefficient
PA	Performance assessment
TcO_4^-	Pertechnetate
SRS	Savannah River Site
Tc	Technetium
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions

1.0 EXECUTIVE SUMMARY

Performance assessments (PAs) are risk calculations used to estimate the amount of low-level radioactive waste that can be disposed at DOE sites. Distribution coefficients (K_d values) are input parameters used in PA calculations to provide a measure of radionuclide sorption to sediment; the greater the K_d value, the greater the sorption and the slower the estimated movement of the radionuclide through sediment. Understanding and quantifying K_d value variability is important for estimating the uncertainty of PA calculations. Without this information, it is necessary to make overly conservative estimates about the possible limits of K_d values, which in turn may increase disposal costs. Finally, technetium is commonly found to be amongst the radionuclides posing potential risk at waste disposal locations because it is believed to be highly mobile in its anionic form (pertechnetate, TcO_4^-), it exists in relatively high concentrations in SRS waste, and it has a long half-life (213,000 years). The objectives of this laboratory study were to determine under SRS environmental conditions: 1) whether and to what extent TcO_4^- sorbs to sediments, 2) the range of Tc K_d values, 3) the distribution (normal or log-normal) of Tc K_d values, and 4) how strongly Tc sorbs to SRS sediments through desorption experiments. Objective 3, to identify the Tc K_d distribution is important because it provides a statistical description that influences stochastic modeling of estimated risk.

The approach taken was to collect 26 sediments from a non-radioactive containing sediment core collected from E-Area, measure Tc K_d values and then perform statistical analysis to describe the measured Tc K_d values. The mean K_d value was 3.4 ± 0.5 mL/g and ranged from -2.9 to 11.2 mL/g. The data did not have a Normal distribution (as defined by the Shapiro-Wilk's Statistic) and had a 95-percentile range of 2.4 to 4.4 mL/g. The E-Area subsurface is subdivided into three hydrostratigraphic layers: Upper Vadose Zone (11 to 30 ft depth), Lower Vadose Zone (30 to 51 ft depth), and aquifer (51 to 95 ft depth). The Upper Vadose Zone generally contains more clay than the Lower Vadose Zone, and the Aquifer tends to be made up of mostly sand layers with clay strata. The mean K_d values of each of these zones did not differ significantly and the K_d values from each zone were not from the Normal distribution. The ranges of values were greatest in the Upper Vadose Zone and least in the Lower Vadose Zone.

Previous Best Estimate Tc K_d values for Sandy Sediment and Clayey Sediment were 0.1 and 0.2 mL/g, respectively (Kaplan 2007a). A more thorough review indicates that the Best Estimates for Sandy Sediment is 0.1 mL/g and for Clayey Sediment is 0.8 mL/g (Kaplan 2007b). This current dataset greatly increases the number of Tc K_d values measured with SRS sediments, but perhaps more importantly, provides a better estimate for E-Area sediments, and provides a measure of Tc K_d distributions. Based on this dataset, the best overall Tc K_d value for E-Area is the mean, 3.4 mL/g, with a log-normal distribution between the 95 percentile values of 2.4 to 4.4 mL/g.

This document version differs from the earlier version, SRNS-STI-2008-00286, in that it includes some editorial corrections. This version does not contain any technical changes or changes to the conclusions presented in the earlier version.

2.0 INTRODUCTION

There have been four previous TcO_4^- sorption studies conducted with SRS sediments (Routson et al. 1977, Oblath 1983, Kaplan 2003, Kaplan and Serkiz 2006). Additionally, Kaplan (2007) conducted a critical review of these data. Of these four studies, the Routson et al. (1977) study does not provide much insight into the geochemistry of Tc at the SRS because varying levels of dissolved carbonate were added to the aqueous phase. Essentially no aqueous carbonate exists in the E-Area groundwater. Pertinent information regarding the three other experiments, including their measured K_d values, are presented in Table 1.

Oblath (1983) reported K_d values that ranged from 0.10 to 1.32 mL/g (#1 – #10 in Table 1). He concluded that there was a positive correlation between clay content and TcO_4^- (pertechnetate; the primary form of Tc expected to exist in the SRS environment) K_d values. TcO_4^- K_d values did not change much as a function of water chemistry (Eh and Fe^{2+}) or sediment organic carbon content (but none of the sediments tested had especially high organic carbon concentrations). He also observed that K_d values measured by column studies tended to be lower than those measured by batch studies. This difference between column and batch studies is commonly attributed to the columns being flushed with the Tc-spiked solution at a rate that does not permit the Tc to come to equilibrium with the sediment. It is difficult to experimentally obtain sufficiently slow flow rates that simulate groundwater conditions, especially in clayey sediments. When contact time is too fast, the column experiment will underestimate the true K_d value. Equally important, batch sorption techniques permit complete mixing of the sediment, water, and Tc system, thereby promoting greater sorption than column studies.

Kaplan and Serkiz (2006) used rhenium (as ReO_4^-) as a non-radiological chemical surrogate for pertechnetate (TcO_4^-) for measuring K_d values of two SRS sediments. Sediment type, pH and organic carbon concentrations were varied in this study. Consistent with the results of Oblath (1983), they observed that the clayey sediment (#11 – #13 in Table 1) sorbed more ReO_4^- than the sandy sediment (#14 – #16 in Table 1). Typical anion sorption behavior (i.e., sorption should increase as pH decreases) was not seen but concentration of dissolved organic C did influence the Tc K_d values (Kaplan and Serkiz 2006). Kaplan (2003) measured Tc K_d of two sediments as a function of pH (#17 – #20 in Table 1). Both sediments had low clay contents 5 – 6 wt-% and sorbed only trace amounts of Tc at pH levels below natural levels (i.e., pH 5.3 for these particular sediments), and these sediments sorb no Tc at pH levels above their natural pH levels.

In a literature review of 143 Tc K_d values, of which few involved SRS sediments, Sheppard and Thibault (1990) observed a trend between Tc K_d values and sediment texture. They suggested the following K_d values:

Sandy sediment (≥70% sand):	0.1 mL/g
Loam sediment (1:1:1 sand:silt:clay):	0.1 mL/g
Clayey sediment (≥35% clay):	1 mL/g

Organic (≥30% organic matter):   1 mL/g

In summary, these studies indicate that Tc K_d values change as a function of sediment texture. The iron oxide phases associated with the clay size fraction are likely responsible for much of the TcO_4^- sorption. SRS subsurface sediments typically contain high concentrations of surface Fe coatings (Looney et al. 1990). In a site-wide survey, SRS sediments range from 0.1 to 8 wt-% Fe, with a median of 0.8 wt-% Fe. Sandy textured sediments also tend to have some sorption, albeit very little, and in some environments they have no Tc sorption, especially at pH levels above background. Tc K_d values also tend to decrease in environments where the ionic strength is high, such as near a waste form.

Based on these site-specific Tc K_d values, Kaplan (2007a) recommended using 0.1 mL/g in sandy sediment, and 0.2 mL/g in clayey sediment. In a more detailed review, Kaplan and Millings (2006) recommended similar K_d values of 0.2 mL/g in sandy sediment and 1.3 mL/g in clayey sediment (summarized in Table 2). In a third review, Kaplan (2007) supported the use of non-zero Tc K_d values in the SRS subsurface.

The objectives of this laboratory study were to determine under SRS environmental conditions:

1. whether and to what extent TcO_4^- sorbs to sediments,
2. the range of Tc K_d values,
3. the distribution (normal or log-normal) of Tc K_d values, and
4. how strongly Tc sorbs to SRS sediments through desorption experiments.

The approach taken was to measure TcO_4^- K_d values of 26 sediments originating from an E-Area coring and then do statistical analysis to describe the distributions of TcO_4^- K_d values. The desorption experiment (Objective 4) involved taking some of the sediments that had TcO_4^- sorbed to them as part of the (ad)sorption K_d test, add competing NO_3^- and CO_3^{2-} anions, and then measure the amount of TcO_4^- that desorbed.

Table 1. Site-specific TcO$_4^-$ K$_d$ Values.

ID#	Kd (mL/g)	Solid	Liquid	Experimental	Ref.[a]
1	0.23	SRS Old Burial Ground Sediment (PD05): within ^{3}H plume, 55 – 56 ft deep, 10% clay/silt + 90% sand	SRS GW	Column	1
2	0.14	SRS Old Burial Ground Sediment (PD05)l: within ^{3}H plume, 57 - 58 ft deep, 10% clay/silt + 90% sand	SRS GW	Column	1
3	0.17	SRS Old Burial Ground Sediment (SDS-5), 35 – 37 ft 10% clay/silt, 90% sand	SRS GW	Column	1
4	0.33	SRS Old Burial Ground Sediment (SDS-5), 64 – 66 ft 30% clay/silt, 70% sand	SRS GW	Column	1
5	0.10	SRS Old Burial Ground Sediment (BG #1) Sediment: 15% clay/silt + 85% sand	SRS GW	Batch	1
6	1.16	SRS Old Burial Ground Sediment (BG #3): 50% clay/silt + 49% sand	SRS GW	Batch	1
7	1.31	SRS Old Burial Ground Sediment (BG #4): 49% clay/silt + 50% sand	SRS GW	Batch	1
8	1.32	SRS Old Burial Ground Sediment (BG #5): 48% clay/silt + 52% sand	SRS GW	Batch	1
9	0.16	SRS Old Burial Ground Sediment (PD05): as #8	D.I. Water	Batch	1
10	0.36	SRS Old Burial Ground Sediment (PD05): as #8	SRS GW	Batch	1
11	0.1	SRS sediment: Clayey sediment; Sand / Silt/Clay; 58%/ 30% /12%; pH 3.9	Groundwater with varying amounts of organic C.	Batch Re tests; ReO$_4^- \approx$ TcO$_4^-$	2
12	0.2	Same as #11, except pH 5.3 (~background)	(same as above)	(same as above)	2
13	0.0	Same as #11, except pH 6.7	(same as above)	(same as above)	2
14	-0.1[b]	SRS sediment: Sandy sediment; Sand / Silt/Clay; 96%/ 0% /4%; background pH 3.9	(same as above)	(same as above)	2
15	-0.1[b]	Same as #14, except pH 5.3 (~background)	(same as above)	(same as above)	2
16	0.0	Same as #14, except pH 6.7	(same as above)	(same as above)	2
17	<0.11	Loamy Sand SRS wetland sediment: 79%/14%/6% sand/silt/clay, high in organic matter (1395 ppm org.-C) pH 3.7 to 4.3.	SRS groundwater	Batch, varied pH: K$_d$s decreased with increased pH (Natural sediment pH = 4.16)	3
18	0	Same as #17, except pH 4.3 to 6.8	(same as above)	(same as above)	3
19	0 to <0.15	Loamy Sand SRS subsurface upland sediment: 80%/15%/5% sand/silt/clay, low in organic matter (<200 ppm org.-C) pH = 2.4 to 4.0	(same as above)	(same as above; except natural sediment pH = 5.0)	3
20	0	Same as #19, except pH > 4.0	(same as above)	(same as above)	3

[a] 1 = Oblath 1983; 2 = Kaplan and Serkiz 2006; 3 = Kaplan 2003
[b] Negative K$_d$ values are possible and have physical meaning (anion exclusion), but for these experiments, they are the result of analytical variability.

Table 2. Tc K_d Values of Sandy and Clayey Sediments Measured at the SRS (modified from Kaplan 2007b).

Sandy Sediment[a]		Clayey Sediment[a]	
ID# in Table 1	K_d (mL/g)	ID# in Table 1	K_d (mL/g)
1	0.23	6	1.16
2	0.14	7	1.31
3	0.17	8	1.32
4	0.33	9	0.16
5	0.1	10	0.36
15	-0.1	12	0.2
18	0		
Average	**0.12**	**Average**	**0.75**

[a] Did not include K_d values from studies where the pH had been experimentally changed from background levels (ID# 11, 13, 14, 16, 17, 19, and 20). A sandy sediment was defined as containing ≥70% sand and a clayey sediment was defined as containing ≥35% clay. These definitions were selected to be consistent with the largest compendium of K_d values, Sheppard and Thibault (1990).

3.0 MATERIALS AND METHODS

A detailed description of the materials and methods are presented in Appendix A. The following sections contain a brief description, sufficient to permit understanding the results. Field sediment sampling, K_d measurements, ^{99}Tc measurements, and statistics were conducted by SRNL researchers (D. Kaplan, K. Roberts, and G. Shine). Sediment characterization was conducted by a Savannah River Ecology Laboratory researcher (J. Seaman) or Clemson University researchers (K. Grogan, R. Fjelds) and has been reported previously in a WSRC report (Grogan et al. 2008).

3.1 K_d VALUE MEASUREMENTS AND SEDIMENT CHARACTERIZATION

Sediment samples were collected from a single borehole (BGO-3A) located in an uncontaminated portion of E-Area. 26 depth-discrete samples were collected from depths ranging from 11 ft (3.3m) to 95 ft (29.0 m) below ground surface.[1] Tc K_d values were determined in duplicate for the 26 sediment samples by measuring the radionuclide concentration in the aqueous phases before and after equilibrating with aqueous Tc. The difference between these two Tc concentrations was assumed to be sorbed onto the sediment surface. A detailed description of the method used to measure the K_d values is presented in Appendix A. Briefly, 1 gram of sediment was added to a centrifuge, followed by 12 mL of SRS groundwater (see Table 9 in Appendix A). This suspension was left on a platform

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[1] Grogan (2008) collected 32 samples, 26 from borehole BGO-3A, and 5 other samples not relevant to this study of K_d distributions.

shaker over night, after which the solids were separated from the liquids, and the liquids were disposed. A second aliquot of 15 mL SRS groundwater was added to the sediment. The samples were then spiked with $^{99}TcO_4^-$, placed on a platform shaker for two days, after which time the solids were separated from the liquids by centrifugation. The resulting solution was analyzed by liquid scintillation. K_d values were calculated by assuming the sorbed fraction was equal to the difference in the aqueous phase ^{99}Tc concentrations before (C_i) and after (C_f) equilibrating with the sediment; this constituted the numerator of the K_d value (Eq. 1). The denominator (Eq. 1) was equal to the aqueous phase ^{99}Tc concentration after equilibrating with the sediment (C_f) multiplied by the particle concentration (Cp) in g/mL

$$K_d = \frac{(C_i - C_f)}{C_f \times Cp} \tag{1}$$

Several sediment properties were also measured to determine if correlations could be made between Tc K_d values and these properties. Sediment properties measured were pH, total Fe/Al/Ti (as measured by X-ray Fluorescence; XRF), dithionite citrate buffer (DCB) extractable Fe/Al/Ti (the approximate Fe, Al, and Ti concentrations in the oxyhydroxide coatings of sediment particles), clay content, and cation exchange capacity.

3.2 DESORPTION OF Tc FROM SEDIMENTS

Six of the sediments used in the sorption test were then reused in a desorption experiment. Approximately 8 mL of either 0.01 M NaCl or Na_2CO_3 were added to each tube. The samples were left on a platform shaker for one week and then the aqueous phase was analyzed for ^{99}Tc by liquid scintillation and for Cl^- (by ion chromatography) and inorganic C (by heating and by difference between the measured total carbon and organic carbon) concentrations. The percentage of Tc desorbed was estimated by calculating the amount sorbed (μg/g sediment) and the concentration of Tc in the aqueous phase after the desorption step (μg/mL x $1/M_{sediment}$ x $Vol_{desorption}$).

3.3 STATISTICAL ANALYSES

The software JMP (version 5.0.1; Cary NC) was used for Analysis of Variance Analysis (ANOVA; to determine if Tc K_d values were different between hydrostratigraphic units), correlations (to determine if Tc K_d values changed in a systematic manner with sediment properties), general descriptive statistics (mean standard error, median, and standard deviation), and distribution analyses (Shapiro-Wilk's statistic; kurtosis, and skewness).

A cumulative distribution graph of the measured Tc K_d data was constructed for the whole core and for each of the three subsurface strata: the Upper Vadose Zone, the Lower Vadose Zone, and the Aquifer Zone (Figure 5). These three hydrostratigraphic layers exist beneath E-Area.

These data were displayed in the form of probability and log-probability plots, which linearize normal and log-normal distributions, respectively. This representation permitted visual identification of the distributions which might be approximated as either normal or log-normal. Regression analyses were conducted between the various K_d values and the sediment characterization parameters. Additional details of the statistical methods used in the study and their interpretation are described in the Results and Discussion section.

4.0 RESULTS AND DISCUSSION

4.1 SEDIMENT CHARACTERIZATION

A sub-surface profile for the BGO-3A core is shown in Figure 1. The sub-surface profile shown in Figure 1 illustrates the presence of several different sediment lenses that occur throughout the BGO-3A core. These lenses represent sediment layers containing sand, clay, and various mixtures of the two. Based on a hydrostratigraphy, this profile has been divided into three zones, the Upper Vadose Zone, Lower Vadose Zone, and Aquifer (Phifer et al. 2006). In this profile, the Upper Vadose Zone lies between 11 to 30 feet depths (286 to 256 ft mean sea level (msl)) and it consists of a relatively large amount of clay compared to the rest of the core. Directly below this region, lies the Lower Vadose Zone which generally contains more sandy textured sediments; this region reaches between 30 and 53 ft depth (256 and 235 ft msl). The water table is at the 54 ft depth. Below the water table, the sub-surface remains primarily sandy with numerous clay lenses to about 100 ft below the surface (186 ft msl) where one final clay layer serves to confine the aquifer. Importantly, based on hydrostratigraphic considerations, the Aquifer Zone is not a unit within itself, but a continuation of the Lower Vadose Zone. However, in this study, the Aquifer Zone was deemed a separate zone because a large amount of variability was measured in this zone, thus the variability was confined to a more limited area, thereby reducing uncertainty in subsequent risk model calculations.

A summary of the sediment characterization data from this core is presented in Table 3. The presence of the various sand and clay layers is confirmed by the sediment characterization data shown in Table 3, particularly the data collected for clay content, iron content, and cation exchange capacity (CEC)[2]. The sediment samples collected from the Upper Vadose Zone (depths between 11 and 30 ft below the surface) generally showed elevated levels of clay, iron, and CEC that correspond to the green and orange layers described in Figure 1. Below this region, there is a noticeable decline in the levels of CEC, clay content, and iron content down to the water table at about 53 ft. Finally, below the water table, there was some significant variability in the measured clay and iron content. As depicted in Figure 1 and quantified in Table 3, the Aquifer Zone consisted largely of sandy sediments with a few samples containing high clay and iron contents. For example, there is a large increase in clay and iron content at 70 ft below the surface (216 ft msl). Similarly, clay and iron lenses were measured for the bottom portion of the core (90 ft to 100 ft) which corresponds to the orange and purple clay bands depicted in Figure 1.

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[2] Cation exchange capacity (milli-equivalents/g) = surface area (m^2/g) x surface charge (milli-equivalents/m^2)
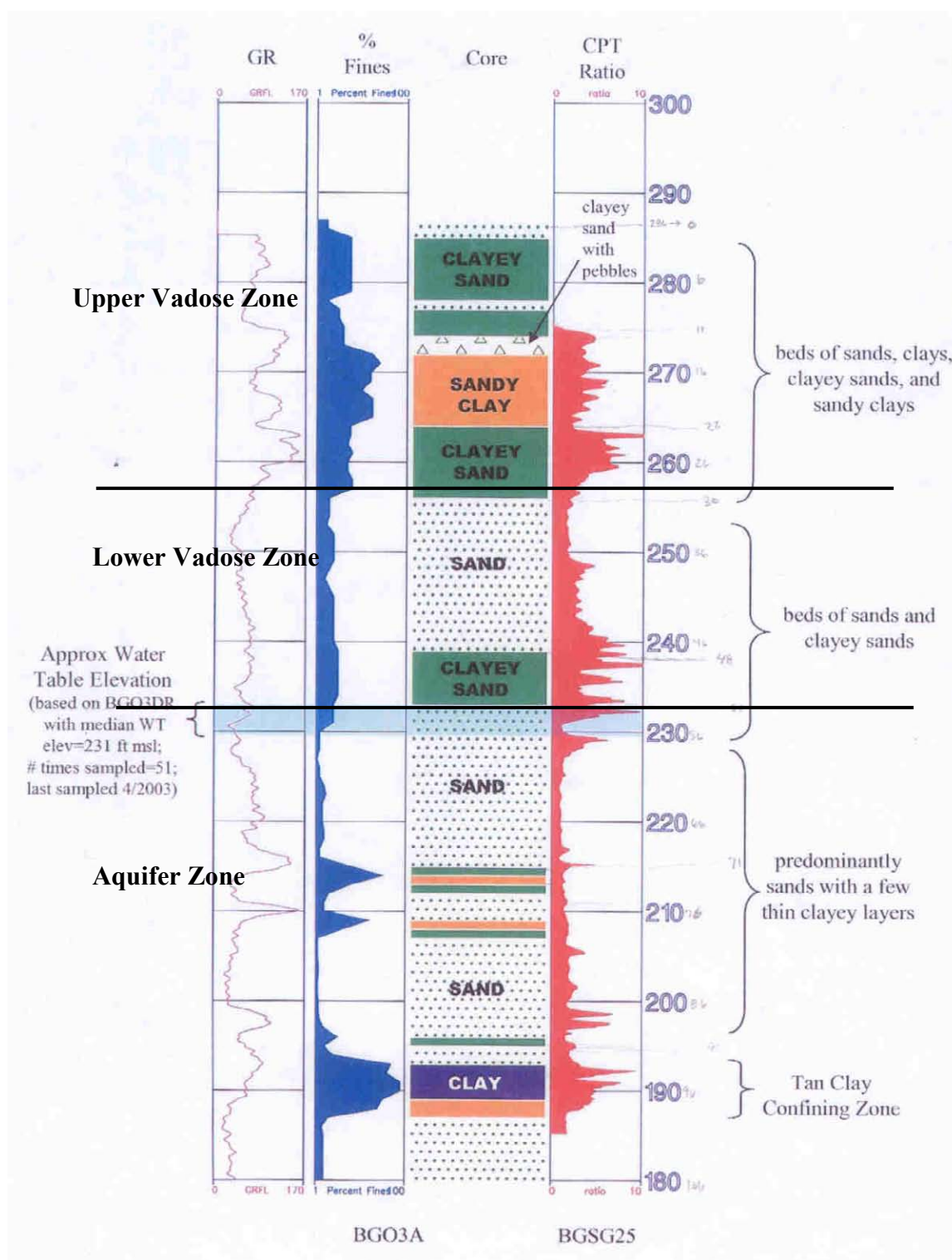
Figure 1. Subsurface Profile of BGO-3A Core. GR is Ground Penetrating Radar Signal, % Fines are the Estimated Percentage of Particles <50-μm based on Casual Observation of Sediment Sample, and CPT (Cone Penetrometer Testing) Ratio is the Ratio of the Pressure Against the Cone Tip (Resistance) to the Drag on the Pipe Just Behind the Cone (Friction). Clay, for instance, has Low Resistance and High Friction.

Table 3. Summary of Tc K_d Values and Sediment Characterization Data for the BGO-3A Borehole (Values Represent Means of Duplicated or Triplicated Measurements).

Sample Depth (ft)[a]	Tc K_d average (mL/g)	Tc Kd stdev (mL/g)	CEC (meq/100g)	Sediment pH	Clay (wt-%)	Al [b] (ppm)	Ti [b] (ppm)	Mn [b] (ppm)	Fe [b] (ppm)
-11	11.2	1.9	2.0	5.1	21.16	1510	14	2	4272
-12.5	4.1	0.5	1.6	5.1	19.45	1424	9	2	2310
-15	4.3	0.3	2.7	6.0	29.05	1550	6	11	5062
-17.5	3.9	0.2	3.3	5.0	49.73	2168	7	4	10183
-20	4.0	0.2	1.5	4.9	18.48	1173	6	11	3554
-25	-2.6	0.1	3.2	5.8	22.71	2240	15	1731	24698
-27	4.0	0.3	1.2	5.0	14.62	1255	10	18	716
-30	4.3	0.3	1.4	5.3	11.56	1104	7	27	429
-32	4.0	0.5	1.0	5.3	7.00	1237	11	7	581
-35	2.9	1.3	1.1	5.4	8.76	1525	7	9	594
-38	4.1	0.1	1.0	5.2	6.31	1601	15	12	814
-40	4.5	0.6	1.6	5.3	9.70	922	6	6	410
-42	1.9	0.1	1.0	5.2	7.16	892	4	34	209
-45	5.2	1.4	1.0	5.2	7.73	1102	6	3	260
-47	4.3	0.0	1.5	5.2	9.16	1223	12	3	327
-50	4.3	0.2	1.6	5.0	9.57	1114	7	3	253
-53	0.7	4.6	1.4	4.9	9.74	1125	6	3	288
-55	4.2	0.2	1.5	5.1	11.03	1161	8	9	363
-58	3.5	0.1	1.1	6.0	2.16	1057	24	11	1160
-60	3.5	0.2	1.0	6.4	0.31	1148	9	20	589
-70	3.9	0.1	1.6	5.0	6.60	1377	14	5	2223
-75	3.6	0.0	1.6	4.8	3.70	1291	9	5	3015
-80	-2.9	0.0	1.2	6.0	2.32	1926	31	27	13619
-85	3.7	0.20	1.1	5.8	1.18	1723	16	14	6566
-90	1.7	0.1	2.9	5.3	7.94	2754	58	169	22696
-95	1.6	0.1	9.3	4.9	21.51	2498	6	204	10462
-100	1.64	0.43	7.4	5.1	12.32	1727	14	47	2991

[a] To convert "Sample Depth" to elevation above mean sea level, as shown in Figure 1, multiply by -1 and then add 274, e.g. the -11 ft sample has an elevation of 284 ft above mean sea level.
[b] dithionite-citrate-buffer extractable; an extract that provides a measure of metals in the surface or hydroxide coatings of sediment particles and does not measure the metal content within the mineral structure.

4.2 Tc K_d VALUES AND THEIR RELATION TO SEDIMENT PROPERTIES

The individual and averaged Tc K_d values are presented in Figure 2 and Table 3. Perhaps the single most important conclusion from this figure is that all but three Tc K_d values were clustered between the mean values of 1.6 and 5.2 mL/g and their standard deviation, as depicted by the error bars in the lower plot in Figure 2, did not overlap with 0 mL/g. The three sediments that had Tc K_d values outside this range were collected from a depth of 11, 25, and 80 ft. These sediments had average K_d values of 11.2 ± 1.9, -2.6 ± 0.1, and -2.9 ± 0.0, respectively. These three values had very small error bars, suggesting that the values were reproducible and represent heterogeneity in the sediment properties, as opposed to analytical error.

The two negative K_d values in the lower graph of Figure 2 likely have physical meaning because the duplicated measurements had near identical results. Negative K_d values have been measured for several monovalent anions, including Cl^- (El-Swaify et al. 1967; Thomas and Swobada 1970; Krupp et al. 1972; James and Rubin 1986), NO_3^- (El Etreiby and Laudelout 1988), and TcO_4^- (Kaplan and Serne 1998). Essentially all sediments in temperate climates have a net negative charge that extends from the surface of the particles into the solution, forming a diffuse double layer (Sposito 1984). When these sediments come in contact with groundwater, the negative surface charge attracts solution cations and repels solution anions. Within the double layer, the anion concentration is near zero at the sediment particle surface and increases with distance until, at the limit of the diffuse double layer, it is equal to anion concentration in the bulk sediment solution. This phenomenon has been referred to as anion exclusion or negative adsorption (Sposito 1984). Anion exclusion can be thought of as the repulsion of anions from particles surfaces and their surrounding double layer. Conversely, it can be thought of as the concentrating of anions in the water beyond the influence of the double layer, i.e., the bulk water. Using Hanford Site subsurface sediments and varying the solution ionic phase, Kaplan and Serne (1998) measured 17 TcO_4^- K_d values ranging from -0.15 to -0.01 mL/g (and one outlier of +0.11 mL/g).

Another reason for believing that the negative K_d values are real and not analytical error is because the mineral composition of at least one sediment, collected at 80 ft depth, contained smectite, a mineral with a large negative charge (Sposito 1984) (Table 4). Smectite, which is not commonly found on the SRS, exists in the tan layer (Grogan et al. 2008). It is quite possible that the thin lens in the Aquifer Zone located at 80 ft depth, originated from the Tan Layer (the underlying clay layer, aquitard, holding up the surface aquifer water) and was displaced upward as a result of more energetic sedimentation processes occurring during the genesis of these sediments (Table 4). The mineralogy of the second sediment with a negative K_d value, from 25 ft depth, was not analyzed; however, it had the greatest Mn (1,731 mg/kg) and Fe (24,698 mg/kg) concentrations, suggesting that high concentrations of Fe- and Mn-oxyhydroxides existed in this sediment. The Fe-oxyhydroxides most abundant in these sediments are goethite, hematite, and amorphous Fe phases (commonly found in SRS sediments at ratios of 6:3:1, respectively). Goethite and amorphous $Fe(OH)_3$ phases have a

zero-point of charge (ZPC)[3] of pH 7.8 to 8.5 (Stumm and Morgan 1996), indicating that they would have a net positive charge at the pH of the sediments (pH 4.8 to 6.4; Table 5) and would be expected to electrostatically attract TcO_4^-. Conversely, Mn exists primarily in sediments as δ-MnO_2, birnessite $((Na,Ca)Mn_7O_{14}$-$8H_2O$, or mixed Fe/Mn/Al-(oxy)hydroxide phases. These minerals have extremely low ZPC, ~pH 2.8 (Stumm and Morgan 1996), suggesting that they would have a strong net negative charge at natural pH levels and would tend to repulse anions, such as TcO_4^-. Finally, our laboratory has measured SRS sediment ZPC values of 5.7 for a subsurface red clayey sediment, and 5.2 for a subsurface sandy sediment (Kaplan et al. 2008). These ZPC values are quite similar to the pH of many of these sediments, indicating that pH-dependent charges were rather limited in these sediments. In summary, the two negative K_d means shown in Figure 2 are likely real and should not be discounted as outliers or physical impossibilities.

The shallowest sample collected at 11 ft had the highest K_d value of 11.2 ± 1.9 mL/g. The geochemical process(es) responsible for this high K_d value are not known (Figure 2).

Descriptive statistics of the K_d values and various sediment properties are presented in Table 5. It shows that the median K_d is 3.93 mL/g, the mean and standard deviation is 3.51 ± 2.55 mL/g, and the range is from -2.93 to 11.19 mL/g. The pH values of these sediments were moderately acidic, 5.3 ± 0.4, with a relatively narrow range of pH 4.8 to 6.4. Cation exchange capacity (CEC), a measure of the total sorption capacity (or a qualitative measure of negative surface charge) had a mean value of 1.9 ± 1.7 meq/100g and also had a narrow range 1.0 to 9.3 meq/100g. The average clay content was 12.0 ± 10.6 wt-%, but its range was very large, 0.3 to 49.7 wt-%. It was unexpected that neither pH, CEC nor clay content was significantly correlated to Tc K_d values (Table 6). However, the Mn and Fe concentrations in the oxide coatings of these sediments, as approximated by the dithionite-citrate buffer extraction, were significantly correlated with Tc K_d values (Figure 3 and Figure 4). It appears that the Mn-DCB/Tc K_d significant correlation was heavily dependent on one value, a weakly poised statistical dataset (Figure 3).

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[3] ZPC is the pH level above which the sediment has a net negative charge and below which the sediment has a net positive charge. Further the pH is from the ZPC, the greater the absolute charge.
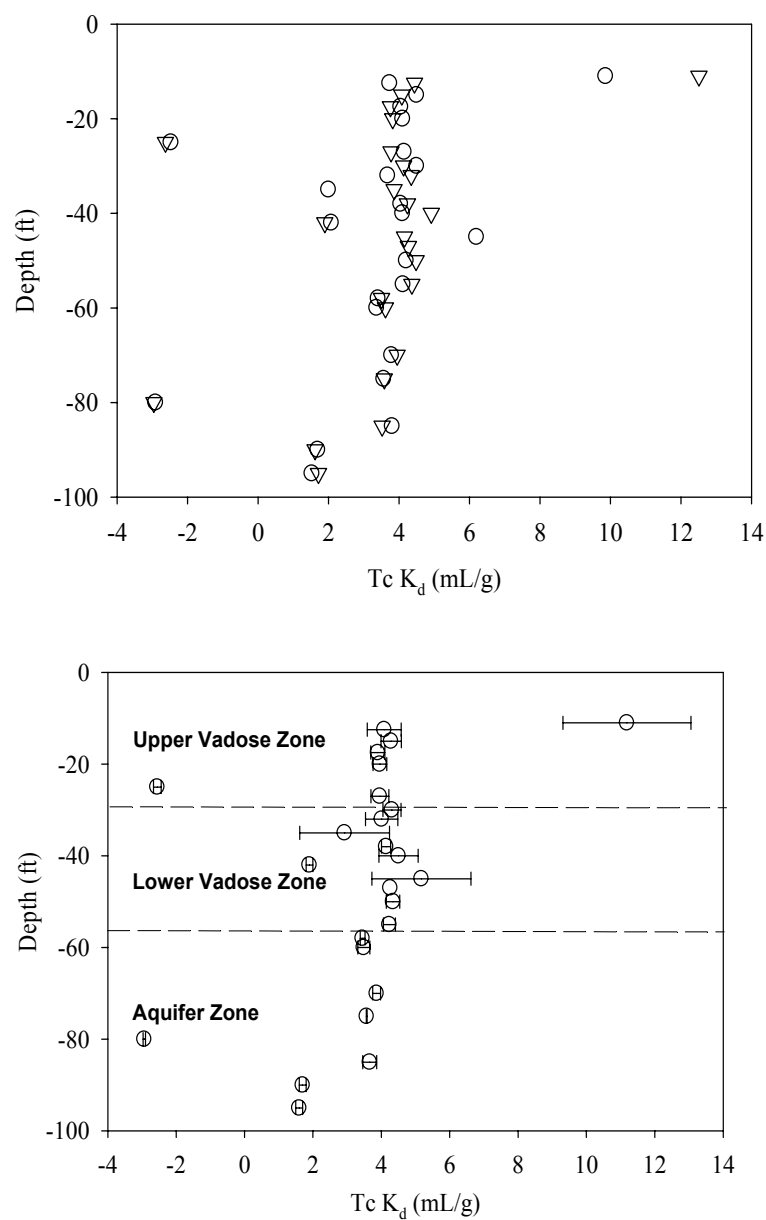
Figure 2. Tc K$_d$ (mL/g) vs. Depth Below Ground Surface (0 ft): Top - First and Second Replicate are Presented, Bottom – Average Tc K$_d$ in Upper Vadose (0 to 32 ft), Lower Vadose Zone (34 to 55 ft), and Aquifer Zone (55 to 80 ft).

Table 4. Sediment Mineralogy Based on XRD and TGA Analysis (Data Taken from Grogen et al. (2008)).

Sample Depth (ft)	Clay Mineralogy[a]	
17.5	kaol(53%)>illite	From the Upper Vadose Zone. Based on sediment appearance and location, this sample is expected to have similar mineralogy as other clayey textured sediments from this hydrostratographic layer.
42	kaol(62%)>illite	From the Lower Vadose Zone. Based on sediment appearance and location, this sample is expected to have similar mineralogy as other sandy textured sediments from this hydrostratographic layer.
80	goe(29%)>kaol(18%)≈smec	From the Aquifer Zone. This sample was selected for mineralogical analysis because it had unusual sorption behavior of metals/rads and Tc (Grogan 2008).
90	smec>goe(21%)≈kaol(18%)>ill	From Aquifer Zone or the underlying Tan Clay "impermeable" layer. Note the high smectite concentration, suggesting unique origin.
95	smec>kaol(27%)>ill>goe	From Aquifer Zone or the underlying Tan Clay "impermeable" layer. Note the high smectite concentration, suggesting unique origin.

[a] goe= goethite, kaol = kaolinite, ill = illite or weathered mica, smec = smectite

Table 5. Descriptive Statistics of Tc K_d Values and Sediment Properties

	Tc Kd (mL/g)	Mn DCB (mg/kg)	Fe DCB (mg/kg)	Ti DCB (mg/kg)	Al DCB (mg/kg)	CEC (meq/100g)	Sediment pH	Clay (wt-%)
Mean	3.38	90.5	4462.3	12.2	1470.6	1.9	5.3	12.3
Std. Error	0.50	66.3	1321.7	2.1	97.6	0.3	0.1	2.1
Median	3.93	10.1	987.1	8.6	1290.5	1.5	5.2	9.4
Std. Deviation	2.55	338.2	6739.3	10.8	497.8	1.7	0.4	10.6
Kurtosis	4.55	24.8	3.8	11.1	1.4	17.0	0.4	5.3
Skewness	-0.01	4.9	2.1	3.1	1.4	3.9	1.1	2.0
Range	14.12	1729.5	24489	51.8	1963.0	8.3	1.6	49.4
Minimum	-2.93	1.8	209.1	4.2	891.9	1.0	4.8	0.3
Maximum	11.19	1731.3	24698	56.0	2854.9	9.3	6.4	49.7
Count	26	26	26	26	26	26	26	26

(a) dithionite-citrate-buffer extractable; an extract that provides a measure of metals in the surface or hydroxide coatings of sediment particles and does not measure the metal content within the mineral structure.

Table 6. Pearson Correlation Coefficients Between Tc K_d Values and Sediment Properties (Data in Table 3)

	Tc Kd	Mn DCB	Fe DCB	Ti DCB	Al DCB	CEC	Sediment pH
Mn DCB	-0.522**						
Fe DCB	-0.575**	0.800**					
Ti DCB	-0.320	0.145	0.431*				
Al DCB	-0.354	0.513**	0.842**	0.410*			
CEC	-0.108	0.532**	0.663**	-0.119	0.630**		
Sediment pH	-0.311	0.242	0.334	0.506*	0.228	-0.019	
Clay (%)	0.108	0.203	0.383	-0.314	0.511*	0.850**	-0.221

(a) dithionite-citrate-buffer extractable; an extract that provides a measure of metals in the surface or hydroxide coatings of sediment particles and does not measure the metal content within the mineral structure.

* significant r value at probability <0.05 and degrees of freedom = 25 is 0.402

** significant r value at probability <0.01 and degrees of freedom = 25 is 0.513
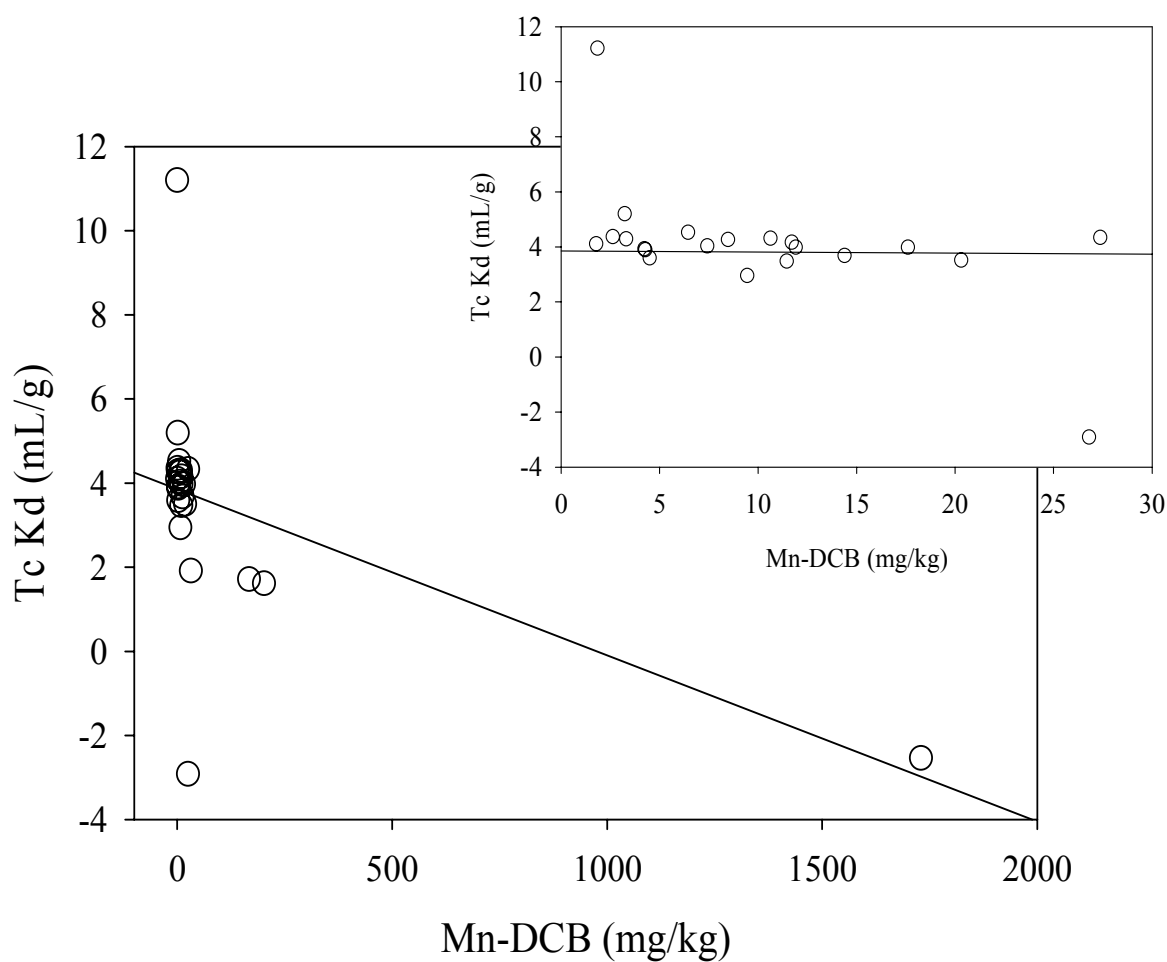
Figure 3. Tc K_d Values as a Function of Mn-DCB. Insert Shows that 23 of the 24 Data Points Indicate that There is no Correlation Between Tc K_d and Mn-DCB Values.
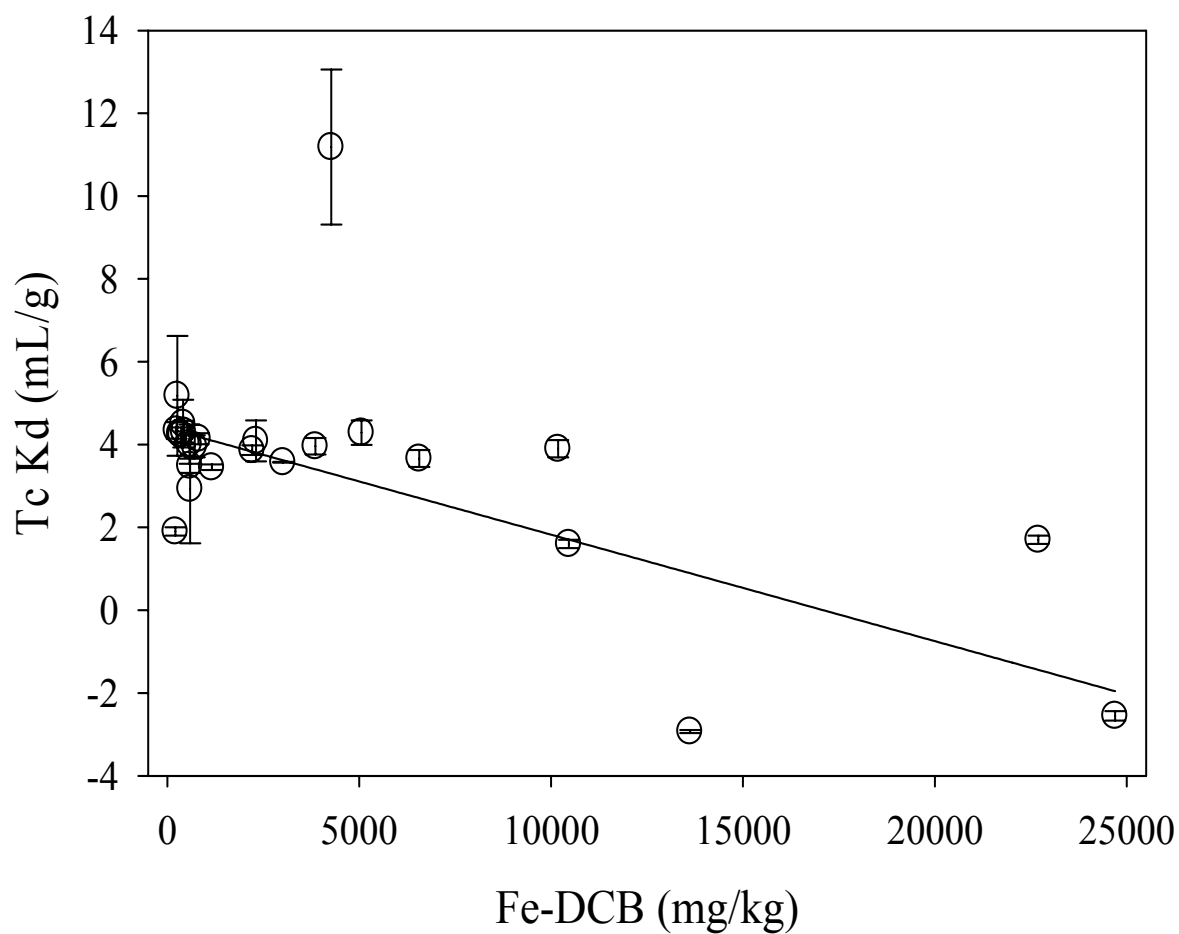
Figure 4. Tc K_d Values as a Function of Fe-DCB.

4.3 DISTRIBUTIONS OF Tc K_d VALUES

The distribution functions of the entire Tc K_d dataset, as well as subsets of the Upper Vadose, Lower Vadose and Aquifer Zones are presented in Figure 5. The Tc K_d data presented in Table 3 were used to make these distribution functions. To help understand the large amount of data presented in Figure 5, a more detailed discussion will be presented of the entire dataset (top plot in Figure 5) to provide an example of interpretation. On the left of each plot included in Figure 5 is the distribution function, where the y-axis is the K_d value and the (unlabelled) x-axis is the number of observations. Drawn over the figures are fits to the normal distribution in red and log-normal distribution in green. In the case of the entire dataset, neither fitted line is a good fit; they both under estimate the number of observations in the central K_d grouping and the extreme K_d groupings. To the right of the distribution function, is a plot describing key statistical moments: the middle of the diamond identifies the mean and the horizontal lines identify the 25 and 75 percentiles. The dots outside the diamonds, identify Tc K_d values that are outliers, i.e., >5 standard deviations from the mean. For the entire dataset, three outliers are identified, 11.2 mL/g (11 ft depth), -2.6 mL/g (25 ft depth), and -2.9 mL/g (80 ft depth) (Table 3). The normal quantile plot is presented on the right. There are 26 dots on this plot representing each Tc K_d value. The red straight line identifies where the data would lie if they were normally distributed and the red arching lines identify the 95% confidence limits from this red line. Comparing the position of the dots to the red line, it can be seen that the dots do not form a straight line; instead they appear to form two lines, suggesting two separate populations. The zone that these K_d values (dots) originate from can be extrapolated from the three other normal quantile lots for the Upper Vadose Zone, Lower Vadose Zone and Aquifer Zone. For example, several of the data points forming the horizontal cluster of points (i.e., those points between 0.25 and 0.90 percentiles), appear to originate in the Upper Vadose and the Aquifer Zones, whereas the data between the 0.25 to 0.05 percentiles (the data forming the slopping cluster of points) originate from the Lower Vadose and Aquifer Zones. Finally, the normal quantile plot for the entire dataset shows the disproportional importance that the three extreme points have on fitting the dataset distribution. Dropping these three points results in a better fit to a log-normal distribution, but we believe the K_d values are real and hold important information about the true Tc K_d value distribution. As such, these values should be included in the statistical description.

The Upper Vadose Zone included eight K_d values and had a range of values that were almost identical to the range for the entire dataset; Upper Vadose Zone – 13.8 mL/g, and for the entire dataset – 14.1 mL/g (Figure 5). The normal and log-normal fits to the distribution functions were poor. The reason for these poor fits can be readily seen in the normal quantile plots (plots right of the histographs in Figure 5), which show the two extreme values and the remaining six values forming a line almost perpendicular to the red line identifying a normal distribution. Of the three subsurface zones, the Lower Vadose Zone showed the closest conformity to normal and log-normal distributions the former being slightly better than the latter. It also had the lowest range of values, from 0.7 to 5.2 mL/g. Finally, the normal and log-normal distributions could not be fit to the Aquifer Zone K_d values. The normal quantile

plot shows poor agreement between the ideal distribution and the actual measured K_d values in this zone.

A statistical test, the Shapiro-Wilk test, was conducted to test the null hypothesis that the data are from the normal distribution (Table 7). The low probability values shown in Table 7 means that the null hypothesis should be rejected, meaning the distribution is not normal. The Tc K_d values were log-transformed to test whether the dataset was log-normally distributed (the two negative values were dropped because there are no logarithmic expressions for negative values). Again, the Shapiro-Wilk statistic for these log transformed distributions indicated that they were not from the log transformed distribution (data not presented). It appears that the use of between 8 to 26 K_d values does not provide enough power for this statistical test. However, it should be noted that the Shapiro-Wilk test is sensitive to even small deviations from normality, thus limiting the value of this statistic test for this application (Mendenhall and Sincich, 2003).

The skewness and kurtosis (Table 7) are two terms that are used to describe a population's distribution. A positive kurtosis indicates a distribution curve with a longer tail than a normal distribution, whereas a negative kurtosis indicates a distribution curve that is flatter than normal. A kurtosis absolute value of $>\pm 3$, i.e., $>|3|$, is considered significant. The kurtosis of the entire dataset, Upper Vadose Zone dataset, and the Aquifer Zone dataset were 4.56, 3.49, and 6.75, respectively (Table 7), indicating that these three datasets have longer tails than a normal distribution. The Lower Vadose dataset had kurtosis values within the range of ± 3. A skewness value $>|3|$, is considered significant and indicates that the data are not symmetrical. Furthermore, a negative skewness indicates tailing of the curve to the left, whereas a positive skewness indicates tailing of the curve to the right. The skewness values for all the datasets were $<|3|$. The largest absolute skewness value was for the Aquifer Zone, -2.58, that had a tail towards the negative values (Table 7).

Given the limited number of measured values for these datasets, between 8 and 26, and the highly sensitive nature of the statistical approach (Shapiro-Wilk test), it was decided to evaluate distributions based on visual inspection (Figure 5). Visual inspections were done by evaluating whether the data best fitted a log normal or normal distribution; particular attention was directed at the normal quantile plots in Figure 5. The entire dataset and the Upper Vadose Zone K_d values appeared to best fit normal distributions, whereas the Lower Vadose Zone and Aquifer Zone appeared to best fit log-normal distributions.

Also included in Table 7 is the 95 percentile range of each of the datasets. Most notable about these data are that they do not include a K_d value of 0 mL/g (or negative K_d values). Perhaps not apparent is why the entire dataset had a lower 95 percentile range than the Upper Vadose or the Aquifer Zones. This occurred because the entire dataset tended to have more data centered on the mean and had more degrees of freedom than these two subsets of the dataset. The 95 percentile ranges for each dataset were (units of mL/g): 2.0 for the entire dataset, 6.1 for the Upper Vadose Zone, 2.2 for the Lower Vadose Zone and 3.5 for the Aquifer Zone. The 95 percentile ranges for Tc K_d values can be expressed in terms of multiples of the mean (3.4 mL/g): Upper Vadose Zone – 3x mean, Lower Vadose Zone – 1x mean, and Aquifer Zone – 2x mean. Grogan et al. (2008) estimated that the range for Am^{3+},

Ca^{2+}, Cs^+, Ce^{3+}, Co^{2+}, Hg^{2+}, Sr^{2+}, Sn^{2+}, and Y^{3+}, were: Upper Vadose Zone 1x mean, Lower Vadose Zone 0.5x mean, and Aquifer Zone – 2x mean. It is unexpected that Grogan et al (2008) values for metals are similar to those for the anion TcO_4^-, with the exception of the Upper Vadose Zone. Processes that control sorption of metals and anions are quite different and for this reason their range of K_d values were expected to differ.

Figure 5. Normal Quantile Plot, Outlier Box Plot, and Distribution Functions for Tc K_d Values for the Entire Core, Upper Vadose Zone, Lower Vadose Zone, and Aquifer.
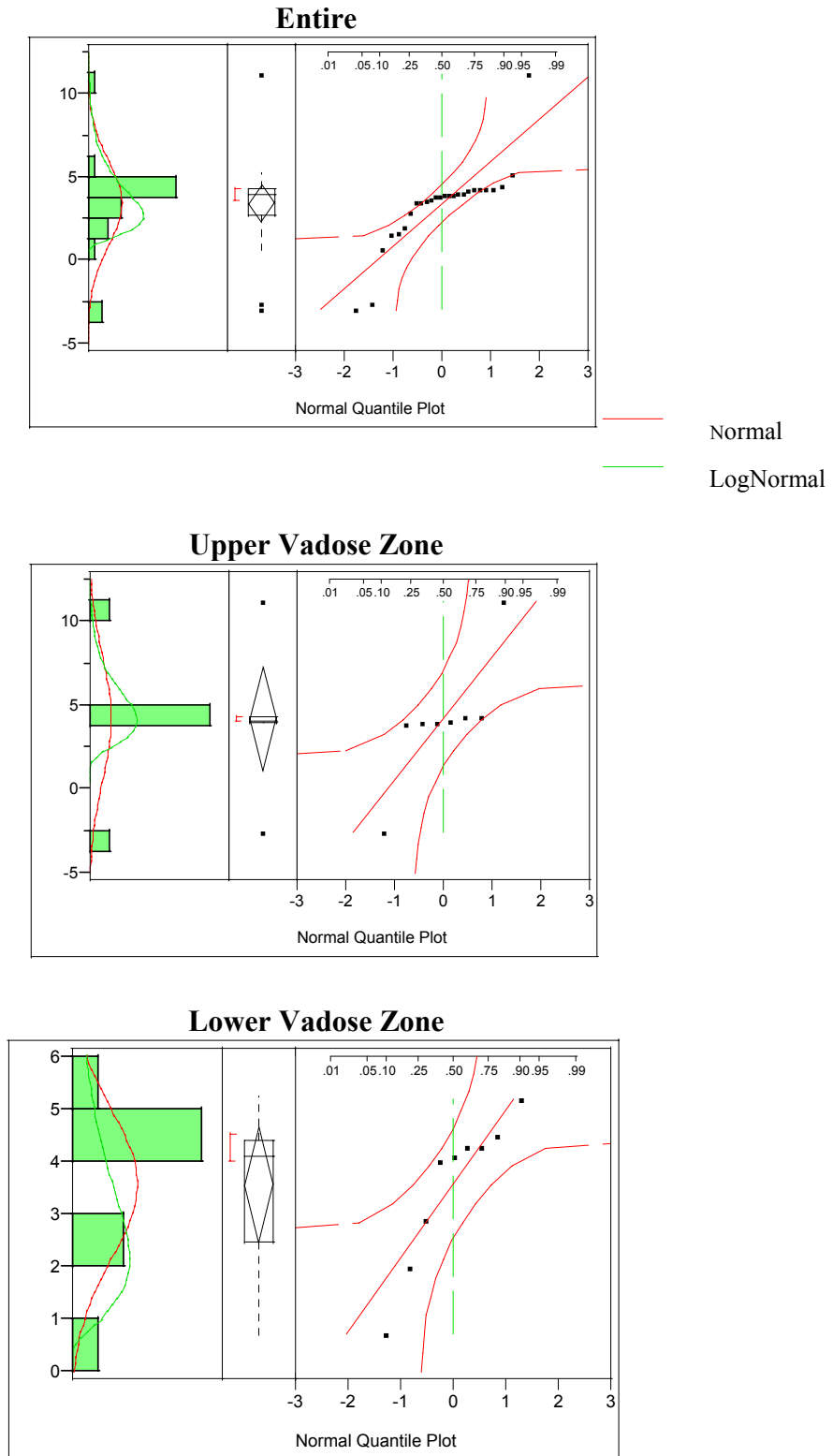
Figure 5 (Continuation). Normal Quantile Plot, Outlier Box Plot, and Distribution Functions for Tc Kd Values for the Entire Core, Upper Vadose Zone, Lower Vadose Zone, and Aquifer.
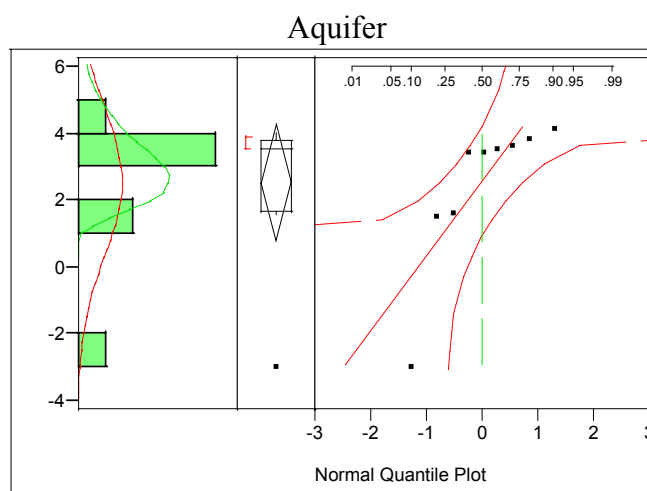
Table 7. Distribution Test Results and 95 Percentile Ranges for Tc K_d Values

Dataset	Skewness	Kurtosis	Shapiro-Wilk Value			Visual[b]	95-percentile	
			W-statistic	p-value	Conclu-sion		Lower	Upper
Entire	-0.15	4.56	0.73	<.0001	Not Normal	Normal	2.4	4.4
Upper Vadose Zone	0.19	3.49	0.77	0.015	Not Normal	Normal	1.1	7.2
Lower Vadose Zone	-1.14	0.31	0.83	0.040	Not Normal	Log-Normal	2.5	4.7
Aquifer Zone	-2.58	6.75	0.52	<.0001	Not Normal	Log-Normal	0.8	4.3

[a] The p-values are the probability that we can reject the null hypothesis stating that the data are from the normal distribution. Small p values indicate we must reject the null hypothesis. For example, a p-value of 0.015 indicates that the null hypothesis can be rejected at the 99.5% confidence level.
[b] Visual tests were conducted by simply looking at distributions presented in Figure 5.

4.4 DESORPTION OF Tc FROM SEDIMENTS

The objective of this task was to determine how strongly the sorbed ^{99}Tc was retained by five sediments. This objective was accomplished by adding two competing anions to the system containing the sorbed Tc. It was anticipated that the two competing anions would promote desorption via anion exchange, thus providing a measure of the percent of Tc that was weakly bound to the sediment. Tc not desorbed by these anions would be considered to be more strongly bound to the sediment. The two competitive anions selected for this study had varying valences and ionic radii: NO_3^- (ionic radius = 165 x 10^{-12} m) and CO_3^{2-} (ionic radius

= 164 x 10^{-12} m). It was anticipated that the divalent carbonate would out-compete the monovalent anions, NO_3^- and TcO_4^-, for exchange sites. 10 mM solutions of $NaNO_3$ and Na_2CO_3 were added to the Tc-bearing sediment. These are relatively high concentrations for uncontaminated groundwater, which commonly contains about a total of 0.1 mM anions (in the appendix see Table 9), but are not uncommon for contaminated groundwater plumes.

The percent of Tc desorbed from the sediments is presented in Figure 6. There was no significant difference ($p \leq 0.05$) between the percent desorbed using nitrate ($32.3 \pm 21.9\%$) and the carbonate ($27.9 \pm 13.9\%$). However, there were very strong correlations between the percentage desorbed and Tc K_d value: % Tc desorbed (nitrate) and Tc K_d had a correlation of 0.980 (n = 6, $p \leq 0.001$), % Tc desorbed (carbonate) and Tc K_d 0.956 (n = 6, $p \leq 0.001$). The geochemical process(es) responsible for these trends are not known.

The sorption sites can be defined as exchange and high-energy:

$$S_{exch\ Tc} = S_{total\ Tc} \times f_{desorb} \tag{2}$$

$$S_{high\text{-}energy\ Tc} = S_{total\ Tc} - S_{exch\ Tc} \tag{3}$$

Where S_{exch}, S_{total}, and $S_{high\text{-}energy}$ are the concentration of exchange sites, total sites, and high energy sites (units = mol/g), and f_{desorb} is the fraction of sorbed Tc that readily desorbs in the presence of a competing anion (% desorbed/100). The exchange sites can be thought of as those that sorb Tc weakly, whereas the high-energy sites are those sites that strongly bind the Tc. The number of high energy sites remained essentially constant in these sediments (columns H and I in Table 8). However, the number of exchange sites steadily increased as Tc sorption increased (columns F and G in Table 8; going down the rows in Table 8, the amount of Tc sorbed decreases). This latter point is especially evident for the sediment with the greatest amount of Tc sorption, the sediment collected at an 11 foot depth and a K_d value of 11.2 mL/g).

The other parameter calculated was the fraction of Tc sorption sites, f_{Tc}:

$$f_{Tc} = S_{total\ Tc}/S_{total\ sediment} \tag{4}$$

where $S_{total\ sediment}$ is the total number of sorption sites in the sediment (mol/g) (column C in Table 8). The fraction of Tc sorption sites is exceeding low. It was not correlated to Tc Sorbed (column B in Table 8).

In summary, these calculations indicate that there were a fixed number of high-energy sites in these sediments, and changes in the number of exchange sites account for differences in the amount of TcO_4^- sorbed to these sediments.
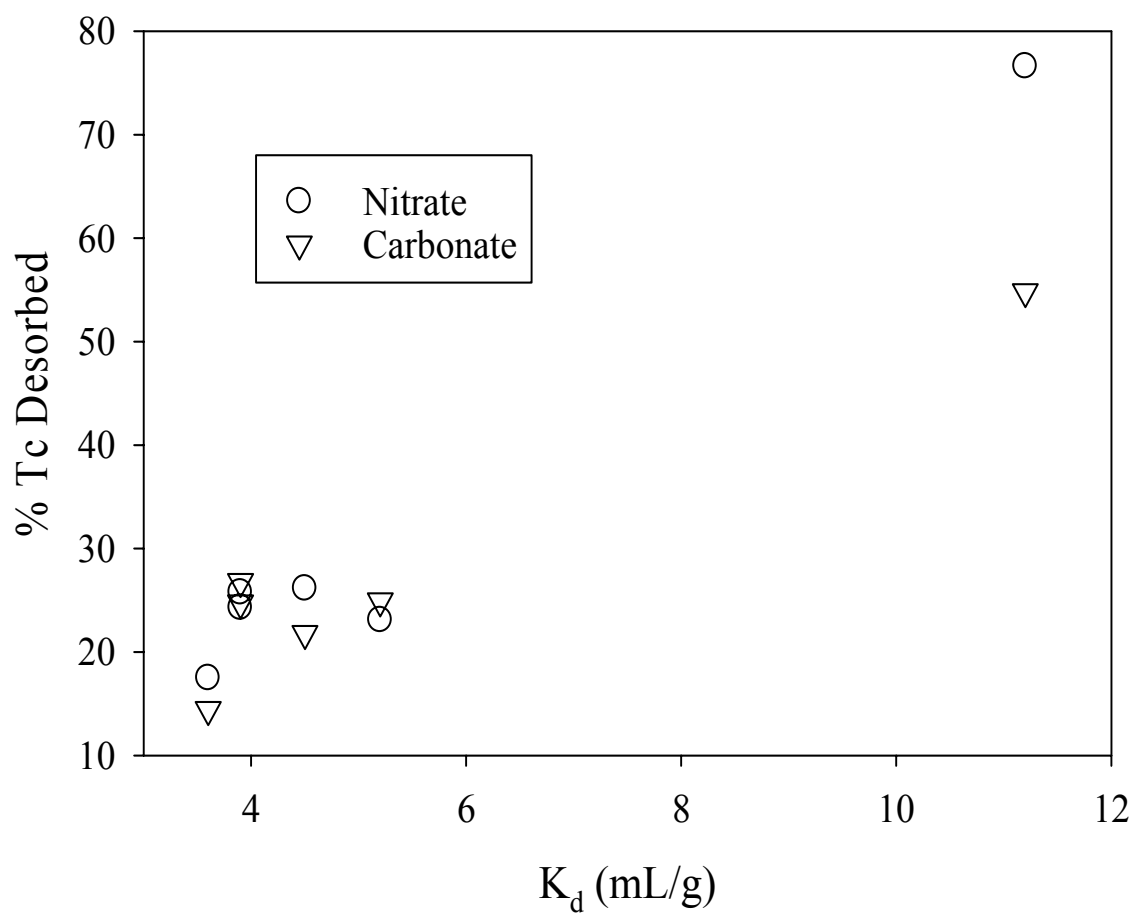
Figure 6. Percent Tc Desorbed using 10 mM Nitrate or Carbonate as a Function of Tc K_d.

Table 8. Technetium Exchangeable and High-Energy Sorption Sites on Sediments.

Column	A	B	C	D	E	F	G	H	I
Sediment Depth (ft)	Total # of Sorption Sites [a] (mol x 10^{-10}/g)	Tc Sorbed[b] (mol x 10^{-10}/g)	Fraction Tc Sorption Sites [c]	% Desorbed – Nitrate [d]	% Desorbed – Carb. [d]	Exch. Sites – Nitrate (mol x 10^{-10}/g)[e]	Exch. Sites – Carb. (mol x 10^{-10}/g)[f]	High Energy Sorption Sites – Nitrate (mol x 10^{-10}/g)[g]	High Energy Sorption Sites – Carb. (mol x 10^{-10}/g)[h]
11	158,000	19.8	1.25E-04	76.6	54.8	15.17	10.85	4.63	10.85
45	61,000	12.8	2.10E-04	23.1	24.9	2.96	3.19	9.84	3.19
40	61,000	11.7	1.92E-04	26.2	21.8	3.07	2.55	8.63	2.55
18	158,000	10.7	6.77E-05	25.8	26.8	2.76	2.87	7.94	2.87
70	6,000	10.5	1.75E-03	24.3	24.7	2.55	2.59	7.95	2.59
75	6,000	9.96	1.66E-03	17.5	14.4	1.74	1.43	8.22	1.43

(a) Total number of sorption sites was estimated by the anion exchange capacity (Unbuffered Salt Extraction Method, Sparks 1996, pp 1218 – 1220). These are estimated values based on measurements of other sediments collected at E-Area with similar clay and Fe-oxide content.

(b) Average from duplicate sorption measurements
(c) Col B/Col A; Equation 3
(d) Measured
(e) Col B x (Col D/100); Equation 1
(f) Col B x (Col E/100); Equation 1
(g) Col B – Col F; Equation 2
(h) Col B – Col G; Equation 2

5.0 CONCLUSIONS

Technetium sorption to 26 sediments within an E-Area sediment core was measured. The average Tc K_d value was 3.4 ± 0.5 mL/g and ranged from -2.9 to 11.2 mL/g. The data were not from normal or log normal distributions. Grouping the K_d data by their hydrostratigraphic layers, i.e., the Upper Vadose, Lower Vadose, and Aquifer Zones, showed that there were no significant differences between mean Tc K_d values of these zones. Relying on trends, rather than statistical tests, it was concluded that the Upper Vadose and Aquifer Zones were best described as log-normally distributed, whereas the Lower Vadose Zone was normally distributed.

The 95 percentile ranges for each dataset were (units of mL/g): 2.0 for the entire dataset, 6.1 for the Upper Vadose Zone, 2.2 for the Lower Vadose Zone, and 3.5 for the Aquifer Zone. The reason the entire dataset had a lower 95 percentile range than those of the Upper Vadose and Aquifer Zones was because there were more values near the mean and a greater number of degrees of freedom. The 95 percentile ranges can be expressed in terms of multiples of the mean (3.4 mL/g): Upper Vadose Zone – 3x mean, Lower Vadose Zone – 1x mean, and Aquifer Zone – 2x mean. Grogan et al. (2008) estimated that the 95 percentile ranges for Am^{3+}, Ca^{2+}, Cs^{+}, Ce^{3+}, Co^{2+}, Hg^{2+}, Sr^{2+}, Sn^{2+}, and Y^{3+}, were: 1x the mean in the Upper Vadose Zone, 0.5x the mean in the Lower Vadose Zone, and 2x the mean in the Aquifer Zone. It is somewhat unexpected that Grogan et al (2008) ranges for metals were similar to the anion, TcO_4^{-}, with the exception of the Upper Vadose Zone. Processes that control sorption of metals and anions are quite different and for this reason their range of K_d values were expected to differ.

Desorption tests indicate that there was a fixed number of high-energy sites in these sediments, and changes in the number of exchange sites account for differences in the amount of TcO_4^{-} sorbed to these sediments. The total number of Tc binding sites was very small compared to the total number of binding sites for anions.

In summary, these data demonstrated that Tc sorbs to SRS sediment, albeit not in large quantities. The 95-percentile range of K_d values does not include 0 mL/g. The distribution of K_d values could not be determined using statistical methods. An appreciably larger dataset would be required to statistically determine their distribution; importantly, a larger dataset would likely result in smaller ranges than those reported in this study. Tc K_d value distributions were approximated as either log-normal in the Upper Vadose Zone and Aquifer Zone and normal in the Lower Vadose Zone.

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7.0 APPENDIX A: RESEARCH AND DEVELOPMENT INSTRUCTIONS AND RAW DATA USED TO CALCULATE K$_d$ VALUES

7.1 R&D DIRECTIONS: TC K$_D$ HETEROGENEITY IN BURIAL GROUND SEDIMENT

7.1.1 Objective:

Measure Tc K$_d$ values of 32 sediments to provide a measure of the Tc K$_d$ heterogeneity in the vadose and surface aquifer formations.

7.1.2 Materials:

1. 32 sediment samples (Table A1)
2. Par Pond Well Water
3. groundwater sample
4. 0.198 µCi/mL ^{99}Tc spike solution: Add 0.16 mL of the original 100 µCi (or 20 µCi/mL) solution to 16 mL of water
5. 15-mL centrifuge tubes
6. 0.1-µm syringe filters
7. 0.1-M HCl
8. pH litmus paper

7.1.3 Methods

1. Record "Tube Tare (g)" weight (without cap) of labeled 15-mL centrifuge tube as identified in Table A1.
2. Add 1.00±0.01-g of sieved sediment to each tube. Weigh and record "Soils (g)"
3. **Equilibrating sediments to the Well Water.** Add 12-mL of Par Pond Well Water to each tube. Put on shaker for overnight. Let sit for 1 hr. Decant liquid. If solids do not separate from the liquid, centrifuge at 15 min 6000 rpm. Then decant liquid. Throw away liquid. Error on the side of leaving liquid in tube rather than accidentally losing clays down the drain. Add 9 mL of Par Pond Well Water to each tube. Also add 9-mL Par Pond Well Water to the three Controls (sample # 157, #158, & #159). Record weight of each tube in "Tube + soils + Equil + GW (g)".
4. **Adding radionuclides to suspension.** Move rack of tubes to rad hood. Add 250-µL of Tc-99 spike solution to each tube. Also add this to the three Controls (sample # 157, #158, & #159). Gently shake or swirl suspensions.
5. **pH adjust suspension.** No pH adjustment is required for this test because the background solution of the ^{99}Tc is 0.001 M KOH, a very weak addition of base.
6. **Equilibrating radionuclides with soil suspension.** Leave samples in rad hood for minimum of 2 days. During this equilibration period, shake rack of tubes twice a day for 10 seconds.
7. Collect liquids by drawing liquids into a syringe and then passing liquid through a 0.1-µm filter.
8. **Tc-99 Analysis.** Submit to Analytical Development Section for liquid scintillation counting of Tc-99.

Safety, Hazards Assessment Package:

SRNL-EST-2006-00-93.

Hazards:

Radionuclides, ~3 mL of strong base

Hazards Mitigation:

Radionuclides: Follow training of Advanced Rad Worker
Strong Base: wear appropriate gloves and as always protective eye ware

Table A1. Sediment descriptions and weights for Tc-99 K_d determinations.

Tube #	Sample #	Rep	Soil pH	Tube Tare (g)	Soil (g)	Tube + Soil + Equil + GW (g)	Tc End of Expt (dpm/mL)
Method Step				(1)	(2)	(3)	
101	**BGO-3A-11**	1	5.1	5.4098	1.00767	16.374	719
102		2		5.41213	1.00969	16.12	624
103	**BGO-3A -12.5**	1	5.1	5.38298	1.00231	16.204	1040
104		2		5.43135	0.99975	16.327	992
105	**BGO-3A -15**	1	6.0	5.41778	1.00128	16.333	988
106		2		5.3863	1.00373	16.407	1020
107	**BGO-3A -17.5**	1	5.0	5.39108	1.00456	16.346	1020
108		2		5.55377	1.00352	16.43	1040
109	**BGO-3A -20**	1	4.9	5.39109	1.00312	16.463	1020
110		2		5.56811	1.00533	16.295	1030
111	**BGO-3A -25**	1	5.8	5.38247	1.00828	16.616	1900
112		2		5.52841	1.00282	16.698	1940
113	**BGO-3A -27**	1	5.0	5.41641	1.00478	16.278	1010
114		2		5.56051	1.00424	16.493	1040
115	**BGO-3A -30**	1	5.3	5.41275	1.0035	16.197	983
116		2		5.62775	1.00044	16.398	1010
117	**BGO-3A -32**	1	5.3	5.56947	1.00498	16.262	1040
118		2		5.62818	1.0007	16.232	989
119	**BGO-3A -35**	1	5.4	5.5403	1.00021	16.187	1190
120		2		5.41791	1.0092	16.287	1030
121	**BGO-3A -38**	1	5.2	5.51688	1.00622	16.159	1010
122		2		5.39018	1.00451	16.138	1000
123	**BGO-3A -40**	1	5.3	5.56608	1.00723	16.345	1010
124		2		5.53811	1.0015	16.321	956
125	**BGO-3A -42**	1	5.2	6.5875	1.0051	17.3655	4870
126		2		6.5990	1.0035	17.3995	4950
127	**BGO-3A -45**	1	5.2	5.36812	1.00158	16.271	883
128		2		5.3898	1.00177	16.238	1010
129	**BGO-3A -47**	1	5.2	5.41009	1.00549	16.288	-

Tube #	Sample #	Rep	Soil pH	Tube Tare (g)	Soil (g)	Tube + Soil + Equil + GW (g)	Tc End of Expt (dpm/mL)
130		2		5.55578	1.00168	16.337	1000
131	**BGO-3A -50**	1	5.0	5.61497	1.00264	16.592	1010
132		2		5.68845	1.00991	16.566	985
133	**BGO-3A -53**	1	4.9	5.59327	1.00285	16.38	1960
134		2		5.41764	1.00924	16.233	1020
135	**BGO-3A -55**	1	5.1	5.55475	1.00823	16.379	1010
136		2		5.39482	1.00464	16.301	996
137	**BGO-3A -58**	1	6.0	5.55573	1.00527	16.189	1060
138		2		5.37612	1.0044	15.928	1050
139	**BGO-3A -60**	1	6.4	5.43184	1.00461	15.948	1060
140		2		5.59826	1.00435	16.11	1040
141	**BGO-3A -70**	1	5.0	5.39333	1.00249	16.003	1030
142		2		5.43435	1.00449	16.14	1020
143	**BGO-3A -75**	1	4.8	5.37874	1.00067	16.064	1050
144		2		5.41851	1.00187	16.162	1050
145	**BGO-3A -80**	1	6.0	5.52928	1.00143	16.26	2050
146		2		5.59181	1.00357	16.3	2070
147	**BGO-3A -85**	1	5.8	5.62937	1.00141	16.28	1030
148		2					1050
149	**BGO-3A -90**	1	5.3	6.5548	1.0045	17.2822	5030
150		2		6.5782	1.0017	17.3445	5070
151	**BGO-3A -95**	1	4.9	6.5525	1.0045	17.3503	5110
152		2		6.6003	1.0024	17.3988	5030
153	**BGO-3A -100**	1	5.1	6.5757	1.001	17.2188	5190
154		2		6.5899	1.0007	17.1122	4910
157	**No sediment control**	1					2.11E+03
158		2					1.06E+03
159		3					1.14E+03
161	**No sed. Cont. – 2nd Trial**	1					5950
162		2					5870
Bold italicized Font Tube # were part of second set of test runs.							

7.2 R&D DIRECTIONS: MEASURING DESORPTION OF Tc-99 ON SRS SEDIMENTS

PI:
> Dan Kaplan/ Kim Roberts

Date:
> 6/9/08

HAP:
> SRNL-EST-2006-00093

Hazards:
> Radionuclides

Hazards Mitigation:

> Radionuclides: Follow training of Advanced Rad Worker

7.2.1 Objectives

Determine how strongly the sorbed ^{99}Tc is retained by these geo-sorbents. This will be accomplished by adding varying anions to systems where ^{99}Tc is sorbed. The competitive anions will have varying valences and ionic radii: NO_3^- (ionic radius = 165 x 10^{-12} m) and CO_3^{2-} (ionic radius = 164 x 10^{-12} m).

7.2.2 Materials

1. Selected samples (see Table A1) from Tc-99 Kd sorption experiment
2. 10-mLdisposable syringes
3. 0.1µm syringe filters
4. 0.01 M $NaNO_3$: Pipette 10ml of 0.1M $NaNO_3$ (from C-14 desorption experiment) into 125ml Nalgene bottle and add 90ml DI
5. 0.01M Na_2CO_3: Pipette 10ml of 0.1M Na_2CO_3 (from C-14 desorption experiment) into 125ml Nalgene bottle and add 90ml DI

7.2.3 Methods

1. From Tc-99 sorption experiment bag, pull the 6 samples (and duplicates) as identified in Table A1.
2. Add 8 mL of appropriate $NaNO_3$ or Na_2CO_3 solution, as designated in Table 1
3. Shake sample vigorously my hand for 5 seconds. Weigh and record weight in Table 2.
4. Measure pH with litmus paper and record in Table A2.
5. Shake by hand 3X a day, at the beginning and end of the work day for one week.
6. Let solids settle to separate solids from liquids.
7. Carefully siphon supernatant from 15ml tube and pass through a 0.1µm syringe filter; collecting filtrate in sample bottle to be submitted to Analytical Development section for liquid scintillation counting of Tc-99 and for ion chromatography analysis for nitrate and carbonate analyses.

Table A2. Tc-99 Desorption sample identification and data collected during sample preparation.

ID	Tube # in Kd exp	Exchange Anion	Rep	Tare+ Solid+Inter after Adsorp. (g)	Aq Tc after desorp (dpm/mL)	pH
Instruction step:		2		3		
BGO-3A-11	101	Nitrate	1	17.965	474	5
BGO-3A-11	102	Carbonate	1	17.643	385	10
BGO-3A-17.5	107	Nitrate	1	17.905	92.8	5
BGO-3A-17.5	108	Carbonate	1	17.839	97.7	10
BGO-3A-40	123	Nitrate	1	18.288	93.1	5
BGO-3A-40	124	Carbonate	1	18.028	89.1	10
BGO-3A-45	127	Nitrate	1	18.092	108	5
BGO-3A-45	128	Carbonate	1	17.926	90.8	10
BGO-3A-70	141	Nitrate	1	17.748	83.6	5
BGO-3A-70	142	Carbonate	1	17.704	88.7	10
BGO-3A-75	147	Nitrate	1	17.892	56.9	5
BGO-3A-75	148	Carbonate	1	17.43	49.4	10

Table 9. Groundwater Chemical Composition.

Analyte	Units	Concentration	Method
pH		5.5	Electrode
TIC	ppm	0.713	O.I. Corp Total Organic C
TOC	ppm	0.514	O.I. Corp Total Organic C
Ag, Al, As, Be, Cd, Co, Cr, Fe, K, Mn, Mo, Ni, P, Pb, Sb, Se, Sn, Ti, U, W, Zn	ppm	BDL	ICP-AES
B	ppm	0.15	ICP-AES
Ba	ppm	0.0027	ICP-AES
Ca	ppm	0.402	ICP-AES
Cu	ppm	0.003	ICP-AES
Mg	ppm	0.29	ICP-AES
Si	ppm	3.02	ICP-AES
Sr	ppm	0.003	ICP-AES
Li	ppb	0.21	ICP-MS
Na	ppb	154.26	ICP-MS
K	ppb	182.72	ICP-MS
Mn	ppb	1.6534	ICP-MS
Fe	ppb	0.056	ICP-MS
Al	ppb	1.39	ICP-MS
Cr	ppb	0.0049	ICP-MS
Co	ppb	0.167	ICP-MS
Ni	ppb	0.468	ICP-MS
Zn	ppb	3.13	ICP-MS
Cu	ppb	18.60	ICP-MS
As	ppb	0.082	ICP-MS
Sr	ppb	4.29	ICP-MS
Mo	ppb	0.76	ICP-MS
Ag	ppb	0.10	ICP-MS
Sn	ppb	0.19	ICP-MS
Ba	ppb	8.16	ICP-MS
Pb	ppb	1.31	ICP-MS
Cl^-	ppm	2.67	Bran-Lubbe Wet Chemistry
NH_4^+	ppm	0	Bran-Lubbe Wet Chemistry
PO_4^{3-}	ppm	<0.0012	Bran-Lubbe Wet Chemistry
Total P	ppm	0	Bran-Lubbe Wet Chemistry
$NO_3 + NO_2$	ppm	0.8319	Bran-Lubbe Wet Chemistry
Total N	ppm	0.795	Bran-Lubbe Wet Chemistry
NO_2	ppm	0	Bran-Lubbe Wet Chemistry
SO_4^{2-}	ppm	<0.5556	Bran-Lubbe Wet Chemistry

Table 10. Inorganic Carbon and Nitrate Concentrations Measured in No-Sediment Control Samples During the Tc Desorption Experiment in Which 10 mM-NaNO$_3$ or -Na$_2$CO$_3$ was Added.

Sediment Depth (ft)	Anion Exchanger	Concentration added (mg/L)
-11	Nitrate	599
	Inorganic Carbon[a]	650
-18	Nitrate	577
	Inorganic Carbon	620
-40	Nitrate	586
	Inorganic Carbon	620
-45	Nitrate	584
	Inorganic Carbon	570
-70	Nitrate	606
	Inorganic Carbon	625
-75	Nitrate	612
	Inorganic Carbon	645

[a] Inorganic Carbon (in units of mg/L C) was measured for the carbonate treatments.

7.3 SEDIMENT CHARACTERIZATION METHODS

Another major task for this study was the characterization of the sediment samples collected from the E-Area as well as the lysimeter control sediment. This characterization included determination of clay fraction, iron oxide content, general iron, titanium, and manganese content, as well as cation exchange capacity and sediment pH. Clay Fraction Determination

The clay fraction for each sediment sample was determined using the micropipette method developed by Miller and Miller (1987) and Burt et al. (1993). To begin the analysis, each sediment sample was passed through a 2 mm screen. Four grams of each sediment was then treated with 10 mL of water and 10 mL of a dispersing agent (5 g/L sodium hexametaphosphate) in a 50 mL centrifuge tube. The mixture was then placed on a shaker and mixed for 2 hours. After this time, 20 mL of water was added to each sample, and the solutions were shaken by hand to ensure that all sediment particles were in solution. The solutions were then placed in a rack and allowed to settle for approximately 1 hour and 50 minutes. After settling a micropipette was used to remove 5 mL of the suspension from the middle of the tube. This 5 mL aliquot was then injected into a pre-weighed aluminum pan. Finally, the aliquot was oven-dried and weighed to determine clay content. Two trials were completed for each of the samples form the BGO-3A core and for the lysimeter control sediment. No trials were completed for any of the sediments from BGX-2B or BGX-11D due to sample scarcity.

7.3.1 Iron Oxide Extraction and Analysis

The iron oxide content of each of the sediment samples was determined using the extraction method developed by Kunze (1986) and Mehra (1960). To begin, 5 g of each sediment were measured into labeled 50 mL centrifuge tubes. Twenty-five mL of CDB solution (0.27 M sodium-citrate dehydrate/0.11 M sodium bicarbonate) was then added to each tube. The sediment suspensions were then heated in a water bath at 80°C. Once heated, 0.75 g of sodium dithionite was added to each solution and stirred continuously for approximately 1 minute. Each suspension was then stirred intermittently for the next 15 minutes under a fume hood. The tubes were then balanced with CDB solution and centrifuged at 10,000 rpm for 15 minutes. After centrifugation the supernatant was decanted into a labeled 100 mL volumetric flask. The remaining solid was then washed with 25 mL of CDB solution, shaken, centrifuged, and decanted into the appropriate volumetric flask in order to remove any residual iron. This wash was then repeated one final time. After combining the extracts, CDB solution was used to dilute the extraction volume in the flask to 100 mL. An aliquot of this dilution was then acidified with 10% HNO_3 and analyzed with ICP-MS. Three trials were completed for each sediment sample.

8.0 APPENDIX B: STATISTICS OF CALCULATE K$_d$ VALUES

Table 11. Distribution of Entire, Upper Vadose Zone, Lower Vadoze Zone, and Aquifer Tc K$_d$ Values.

		Entire			Upper Vadose Zone			Lower Vadose Zone			Aquifer	
Quan-tiles	100.0%	maximum	11.20	100.0%	maximum	11.20	100.0%	maximum	5.20	100.0%	maximum	4.20
	99.5%		11.20	99.5%		11.20	99.5%		5.20	99.5%		4.20
	97.5%		11.20	97.5%		11.20	97.5%		5.20	97.5%		4.20
	90.0%		4.71	90.0%		11.20	90.0%		5.20	90.0%		4.20
	75.0%	quartile	4.30	75.0%	quartile	4.30	75.0%	quartile	4.40	75.0%	quartile	3.80
	50.0%	median	3.95	50.0%	median	4.05	50.0%	median	4.10	50.0%	median	3.50
	25.0%	quartile	2.67	25.0%	quartile	3.92	25.0%	quartile	2.45	25.0%	quartile	1.65
	10.0%		-0.29	10.0%		-2.60	10.0%		0.70	10.0%		-2.90
	2.5%		-2.90	2.5%		-2.60	2.5%		0.70	2.5%		-2.90
	0.5%		-2.90	0.5%		-2.60	0.5%		0.70	0.5%		-2.90
	0.0%	minimum	-2.90	0.0%	minimum	-2.60	0.0%	minimum	0.70	0.0%	minimum	-2.90
Mo-ments	Mean		3.38	Mean		4.15	Mean		3.56	Mean		2.53
	Std Dev		2.55	Std Dev		3.69	Std Dev		1.42	Std Dev		2.24
	Std Err Mean		0.50	Std Err Mean		1.31	Std Err Mean		0.47	Std Err Mean		0.75
	upper 95% Mean		4.42	upper 95% Mean		7.24	upper 95% Mean		4.65	upper 95% Mean		4.25
	lower 95% Mean		2.35	lower 95% Mean		1.07	lower 95% Mean		2.46	lower 95% Mean		0.81
	# observations		26	# observations		8	# observations		9	# observations		9

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