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**Pacific Northwest  
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# Carbon Tetrachloride Partition Coefficients Measured by Aqueous Sorption to Hanford Sediments from Operable Units 200-UP-1 and 200-ZP-1

D. M. Wellman  
R. G. Riley  
E. A. Rodriguez  
A. V. Mitroshkov  
K. E. Parker

September 2007

Prepared for the U.S. Department of Energy  
under Contract DE-AC05-76RL01830



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Richland, Washington 99354



## Summary

In 2004, Fluor Hanford, Inc. (FHI) drilled several groundwater wells within the 200-UP-1 operable unit to monitor plumes that have been the focus of past remediation activities. Thirteen cores taken from three wells (699-30-66, 699-36-70B, and 299-W19-48) were sent to the Pacific Northwest National Laboratory (PNNL) for characterization and quantification of contaminant retardation. These cores were 4 inches in diameter by 6 inches in length, and were collected from depths near the unconfined-aquifer surface (water table) to locations approximately 150 to 180 feet below the water table. Additionally, in 2005 and 2006, FHI drilled several groundwater wells within the 200-ZP-1 operable unit to monitor plumes that have been the focus of past remediation activities. Twelve cores from split-spoon sampling of four of the wells (299-W11-43, 299-W11-86, 299-W14-71, and 299-W14-72) were sent to PNNL for quantification of carbon tetrachloride ( $\text{CCl}_4$ ) sorption. These cores were 4 inches in diameter by 6 inches in length, and were collected from depths near the unconfined aquifer surface (water table) to locations approximately 450 feet below ground surface.

Prior to this work, no site-specific adsorption data (i.e., values of distribution coefficient [ $K_d$ ]) were available for the sediments or key contaminants present in the 200-UP-1 or 200-ZP-1 operable-unit groundwater plume. Selected physical and chemical characteristics of the sediments were determined (e.g., moisture content, particle size, specific surface area and carbon content). Site-specific sorption data for  $\text{CCl}_4$ , with contact times from three to five days, was obtained with the  $< 2$  mm size fractions of uncontaminated sediments taken from these boreholes and the partition coefficients ( $K_d$ ) determined. The magnitude of  $K_d$  values was evaluated in the context of selected sediment characteristics and values of  $\text{CCl}_4$   $K_d$  used in past Hanford assessments.

Organic carbon content, known to influence the magnitude of  $K_d$  values, was low in all sediments ranging from 0.02% to 0.04% in the less than 2 mm fraction. In some of the sediments, organic carbon content was below detection. Silt and clay surface areas ranged from 2 to 25  $\text{m}^2 \text{g}^{-1}$ .

The  $\text{CCl}_4$   $K_d$  values measured for the three 200-UP-1 sediments exhibited bimodal sorption with initial  $K_d$  values (phase 1) ranging from  $2.42 \times 10^{-4} \text{ L Kg}^{-1}$  to  $3.20 \times 10^{-4} \text{ L Kg}^{-1}$ , and phase 2 values approximately  $3.0 \times 10^{-3} \text{ L Kg}^{-1}$  for all sediments. Bimodal-sorption behavior was observed for three 200-ZP-1 sediments, which contained 0.03 - 0.04% organic carbon and a surface area  $> 2 \text{ m}^2 \text{g}^{-1}$  for the silt and clay fraction. Phase 1  $K_d$  values measured for the eight 200-ZP-1 sediments ranged from  $9.65 \times 10^{-6} \text{ L Kg}^{-1}$  to  $5.21 \times 10^{-5} \text{ L Kg}^{-1}$ . For those sediments exhibiting bimodal behavior, phase 2  $K_d$  values ranged from  $1.17 \times 10^{-4} \text{ L Kg}^{-1}$  to  $3.14 \times 10^{-4} \text{ L Kg}^{-1}$ .

Phase-1 200-UP-1  $K_d$  values were approximately 10 times higher than  $K_d$  values measured for 200-ZP-1 sediments. Values of  $K_d$  for sediments from 200-ZP-1 appeared to correlate with organic carbon content for  $\text{CCl}_4$  concentrations  $> 6000 \mu\text{g L}^{-1}$ . No other correlations were readily evident between the sorption of  $\text{CCl}_4$  and physical-sediment characteristics. However, the higher silt and clay contents of the 200-UP-1 sediments (relative to 200-ZP-1 sediments) further suggested the significance of this fraction for yielding higher  $K_d$  values.

Values of  $\text{CCl}_4$   $K_d$  measured in this study are on the lower end of a range of  $\text{CCl}_4$   $K_d$  values estimated from non-Hanford data and used in previous Hanford assessments. These data, along with other recently published data on  $\text{CCl}_4$  desorption  $K_d$  values in Hanford sediments, are scientifically defensible

alternatives for application in future Hanford assessments. This includes an alternative to the most conservative assumption of complete advective transport of CCl<sub>4</sub> in Hanford groundwater (i.e., application of a 0 L kg<sup>-1</sup> value of  $K_d$ ).

## **Acknowledgements**

The authors wish to thank Mark Byrnes and Tom Fogwell (Fluor Hanford, Inc.) for supporting this work.





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## Acronyms and Abbreviations

200-UP-1	Groundwater Operable Unit in 200 W
200-ZP-1	Groundwater Operable Unit in 200 W
ASA	American Standards Association
ASTM	American Society for Testing and Materials
BET	Brunauer-Emmett and Teller Nitrogen Adsorption
$C_f$	Final Concentration of Solute
$C_e$	Final Concentration
$C_o$	Initial Concentration
CI	Confidence Interval
COC	Contaminant of Concern
DOE	Department of Energy
EC	Electrical Conductivity Measure of Salt Content in Fluid
EPA	Environmental Protection Agency
FHI	Fluor Hanford, Inc.
GC-MS	Gas Chromatography-Mass Spectrometry
$K_d$	Distribution Coefficient
PNNL	Pacific Northwest National Laboratory
$S_e$	Contaminant Concentration on Solid Phase



## 1.0 Introduction

Volatile chlorinated hydrocarbon compounds are major constituents contaminating groundwater at U.S. Department of Energy (DOE) installations in the United States (Riley and Zachara 1992). A notable example is a plume at DOE's Hanford site, where 9.8 square kilometers of groundwater is contaminated with carbon tetrachloride ( $\text{CCl}_4$ ) at a level that exceeds the U.S. Environmental Protection Agency's (EPA) drinking-water standard of  $5 \mu\text{g L}^{-1}$  (Hartman et al. 2007). Because of the absence of site-specific experimentally derived data, past assessments addressing the transport of  $\text{CCl}_4$  in Hanford groundwater have assumed advective transport (i.e.,  $0 \text{ L kg}^{-1}$  partition coefficient value [ $K_d$ ] in the transport model) or estimated values of  $K_d$  based on non-Hanford data (Chiaramonte et al. 1996; Bergeron and Cole 2004; Truex et al. 2001).

From 2004 to 2006, Fluor Hanford, Inc. (FHI) drilled groundwater wells within the 200-UP-1 and 200-ZP-1 operable units, respectively, to monitor contaminant plumes that have been the focus of past remediation activities. Sediment cores were collected from these wells (699-36-70B, 299-W19-48, 299-W11-43, 299-W11-86, 299-W14-71, and 299-W14-72) and made available to Pacific Northwest National Laboratory (PNNL) to conduct laboratory sorption experiments, obtaining experimentally derived  $\text{CCl}_4$   $K_d$  on samples from these sediment cores. This report describes those experiments and the findings.



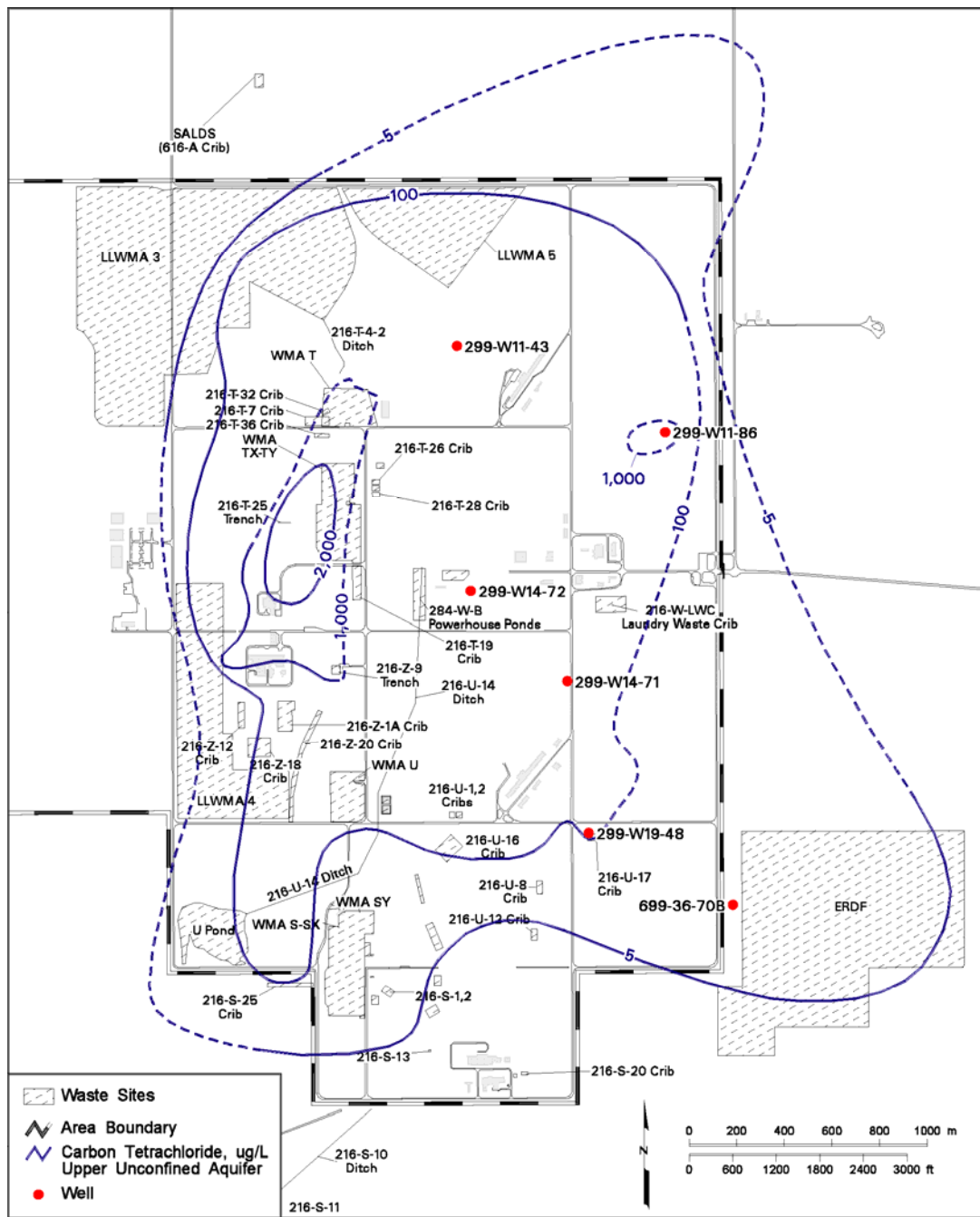
## 2.0 Sediment Sample Sources

Two, one-foot-long split-spoon samplers were used to collect sediment cores from the 200-ZP-1 and 200 UP-1 operable units. Cores within the split-spoon samplers were contained within stainless-steel liners (4 inches in diameter by 6 inches in length with plastic end-caps) collected from the unconfined aquifer of the Hanford site's 200 West Area by Fluor Hanford, Inc., delivered to PNNL for physical and chemical characterization, and use in CCl<sub>4</sub> sorption experiments. The 200-ZP-1 sediment samples were from boreholes 299-W11-43, 299-W11-86, 299-W14-71, and 299-W14-72 in the 200 West Area (Figure 2.1) with depths in the range of 95.7 to 146.9 meters (314 to 482 feet) below ground surface (Table 2.1). The 200-UP-1 sediments were from wells 299-W19-48 and 699-36-708 (Figure 2.1) with depths in the range of 102.8 to 142.6 meters (308 to 428 feet) below ground surface. Details regarding the collection and characterization of sediments from wells 299-W19-48 and 699-36-70B are described in Um et al. (2005).

**Table 2.1.** Sediment Sample Identification and Lithology

Sample Number	Well	Depth (feet)	Lithology
B1D7M3	299-W11-43	364-354	Ringold E: 5% gravel, 90% sand, 5% silt
B1JXB1	299-W11-86	314-316	Upper Ringold E: 40% sand, 5% silt, 55% gravel
B1JXJ6	299-W11-86	398-400	Ringold E gravel: 65% gravel, 20% sand, 15% silt and clay
B1JXJ7	299-W11-86	440-442	Ringold E gravel: 15% silt and clay, 45% sand, 40% gravel
B1JXK0	299-W14-71	322.2-324.2	Ringold E gravel: 50% sand, 30% gravel, 20% mud
B1JXK1	299-W14-71	397.9-399.9	Deeper Ringold gravel: 45% gravel, 35% mud, 20% sand
B1JXK5	299-W14-72	405-407.5	Deeper Ringold E gravel: 60% sand, 40% mud
B1JXK6	299-W14-72	434-436.5	Ringold Lower mud: 100% mud
*B19136 + B19137	699-36-70B	271.5-309	Ringold E
*B19140	699-36-70B	419-419.5	Ringold E
*B19377	299-W19-48	427.5-428	Ringold E

\* Um et al., 2005



**Figure 2.1.** Map of 200W Area, Illustrating CCl<sub>4</sub> Plume and Sample Well Locations.



## 3.0 Sediment Characterization

### 3.1 Sediment Moisture Content

Gravimetric water content of sediment samples was determined using an approved PNNL procedure based on the American Society for Testing and Materials (ASTM) procedure Test Method D2216-98 (ASTM 1998). Representative duplicate subsamples of at least 20 to 80 grams were taken from each core. Sediment samples were placed in tared containers, weighed, and dried for at least 24 hours in an oven at 105°C (221°F) until constant weight was achieved. The gravimetric water content was computed as the percentage change in soil weight before and after oven drying.

### 3.2 Bulk Fraction Distribution Analysis

Dry-sieving and hydrometer methods were used to determine the particle-size distribution for selected core samples. The method is based on the American Society for Testing and Materials procedure *Standard Test Method for Particle-Size Analysis of Soils* (ASTM 2002). The silt and clay, sand, and gravel-size fractions were separated by sieving. The weight percentage of silt-and-clay-size fractions was determined from Stokes' law settling velocities.

Particle density was determined on oven-dried <2 mm fractions using the "Pycnometer Method," as described in American Standards Association (ASA) (1986b) Part 1, Method 14-3. The particle density is an input needed to determine the particle size when using the hydrometer method.

### 3.3 Specific Surface Area

Specific surface area was measured based on the multi-point Brunauer-Emmett-Teller krypton (N<sub>2</sub>)-adsorption method (BET) (Brunauer et al. 1938), using a Quantachrome Autosorb-6B gas sorption system. Grab samples, approximately 0.5 grams, of each of the materials (i.e., the alumina standard, sediment samples) were weighed and placed in tared sample flasks. Flasks containing the samples were heated to 100°C and placed under vacuum (3 μm Hg) for 24 hours. A vacuum was pulled on the sample flasks for 24 hours to remove all physi-sorbed contaminants from the mineral surfaces and provide a clean, solid surface onto which a monolayer of gas molecules would adsorb. The surface area for the sediments was then determined by the adsorption of N<sub>2</sub> on the surface of the sample by:

$$\frac{P}{V_a(P_o - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C} \left( \frac{P}{P_o} \right) \quad (1)$$

where  $V_a$  = quantity of gas adsorbed at pressure ( $P$ )

$V_m$  = quantity of gas adsorbed to form a complete monolayer

$P_o$  = saturation pressure of the gas

$C$  = BET constant.

The values of  $V_m$  and  $C$  are determined by a regression line of the adsorption isotherm plotted

with  $P/V_a(P_o-P)$  versus  $P/P_o$ . The specific surface area of a solid is determined by (Sing et al. 1985):

$$Area = \frac{V_m}{22414} a_m N_A 10^{-20} \quad (2)$$

where  $a_m$  = average area occupied by a single adsorbate molecule

$N_A$  = Avogadro's number.

### 3.4 Total/Inorganic Carbon Analysis

The carbon content of the sediment samples was determined (in duplicate) using ASTM Method D4129-88, Standard Methods for Total and Organic Carbon in Water by High-Temperature Oxidation and by Coulometric Detection (ASTM 1988). Total carbon in all samples was determined using a Shimadzu TOC-V Total Organic Carbon analyzer with combustion at approximately 980°C (1796°F).

The inorganic carbon content of sediment samples (also performed in duplicate) was determined using a Shimadzu TOC-V Total Organic Carbon Analyzer. Soil samples were weighed on a four-place analytical balance and then placed into acid-treated glass tubes. Following placement of sample tubes into the system, a one-minute waiting period allowed the ultrapure-oxygen-carrier gas to remove any carbon dioxide introduced to the system from the atmosphere. Inorganic carbon was released through acid-assisted evolution (50% hydrochloric acid) with heating to 200°C (392°F). Samples were completely covered by the acid to allow full reaction to occur. Ultrapure-oxygen gas swept the resultant carbon dioxide through the equipment to determine inorganic carbon content by coulometric titration. Sample titration readings were performed five minutes following acid addition and again once stability was reached, usually within 10 minutes. Background values were determined and known quantities of calcium carbonate standards were analyzed to verify that the equipment was operating properly. Inorganic carbon content was determined through calculations performed using the microgram-per-sample output data and sample weights.

Organic carbon was calculated as the difference between the measured total and inorganic carbon.

## 4.0 Sorption Test Method

### 4.1 Accelerated Solvent Extraction of Sediments

A DIONEX accelerated solvent-extraction system (ASE-200) was used for the extraction of residual volatile organic compounds from the sediments using methanol as the extraction solvent. Each sample of sediment was placed in an 11-milliliter stainless-steel sample tube, capped at both ends. Both caps had small openings, one to deliver methanol into the tube through the needle and to remove methanol extract. To prevent losses of solutes through the openings, each sediment sample was sandwiched between two layers of clean Ottawa sand. Normally, 13 to 15 grams of the sand was placed at the bottom of the tube, followed by about 20 grams of wet sediment and, on top of the sediment, another 13 to 15 grams of the sand. Tubes were placed in the rotating tray of ASE-200 and heated to 40°C (104°F). Upon reaching 40°C (104°F), 5 milliliters of methanol was injected under pressure into each tube. Following injection, tubes were held five minutes at 40°C (104°F). Following the five-minute hold, methanol, under the high pressure of ultra-high-purity nitrogen, was displaced from the tube and collected in 60-milliliter vials. This cycle was repeated three times. The volume of the extract ranged from 12 to 14 milliliters, depending on the dryness of the sample.

Recovery of CCl<sub>4</sub> from sediments using accelerated solvent extraction was determined for extraction temperatures ranging from 40°C (104°F) to 100°C (212°F). It was found that 40°C (104°F) was optimal for the extraction of CCl<sub>4</sub>. Recovery of aqueous solutions of CCl<sub>4</sub> spiked into sediments was between 82 and 101%, depending on the type of soil.

### 4.2 Analysis of Aqueous Samples by Gas Chromatography-Mass Spectrometry (GC-MS)

The GC-MS was conducted according to standard technical procedures developed by the Pacific Northwest National Laboratory. The water samples were diluted 400-500 times in boiled Milli-Q water and analyzed with a Hewlett Packard 5890 gas chromatograph, fitted with a purge and trap system (P&T, O.I. Analytical, Model 4660), with photoionization (PID, Model 4430) and electrolytic conductivity (ELCD, Model 5320) detectors. Solute compounds were separated on a 105 meter by 0.53 millimeter megabore capillary column (Restek Corporation) and quantified using a four-point calibration. Calibration standards were prepared from a commercial standard consisting of 14 volatile hydrocarbons in methanol (Restek corporation, 502.2 Calibration Mix #2).

### 4.3 Determination of Distribution Coefficient

Values of  $K_d$  were determined in batch experiments for eight sediment samples collected from the ZP-1 Operable Unit.  $K_d$  values were calculated using measurements of CCl<sub>4</sub> in aqueous solution by gas chromatography-mass spectrometry (GC-MS). The sorbed concentration was determined by mass balance, assuming that differences between  $C_o$  and  $C_f$  were due to sorption of CCl<sub>4</sub> to the sediments (ASTM 2001; 2004). The distribution coefficient,  $K_d$ , is defined as:

$$K_d = \frac{(C_o - C_f)M_s}{C_f M_m} \quad (3)$$

where  $C_o$  = initial concentration of the solute ( $\mu\text{g L}^{-1}$ )

$C_f$  = final concentration of the solute ( $\mu\text{g L}^{-1}$ )

$M_s$  = mass of solute in solution ( $\mu\text{g}$ )

$M_m$  = mass of sediments expressed on an oven-dried basis ( $\mu\text{g}$ ).

For all batch isotherm experiments, the solution-to-solid ratio utilized was 1:100 with a three-day contact. Contact time for pervious batch isotherm experiments with 200-UP-1 sediments was five days. After pre-equilibration, a solution containing  $\text{CCl}_4$  in Hanford groundwater was added. Five different initial concentrations,  $C_o$  ( $\mu\text{g L}^{-1}$ ), of  $\text{CCl}_4$  that ranged from 50 to 5000  $\mu\text{g L}^{-1}$  were added to batch-experiment sediment samples. This concentration range included the Environmental Protection Agency Maximum Contaminant Level for  $\text{CCl}_4$  (5  $\mu\text{g L}^{-1}$ ) and higher levels historically observed in the Hanford  $\text{CCl}_4$  groundwater plume. Batch experiments were run in duplicate and included control samples that were free of either sediment or  $\text{CCl}_4$ . Test vessels utilized stop-valve septum caps to prevent volatilization of  $\text{CCl}_4$ .

#### 4.4 Data Analysis

Data from the adsorption experiments were fit with linear, or C-curve, adsorption isotherms. The linear equation has the form (Sparks 1995; Sposito 1989):

$$S_e = K_d C_e \quad (4)$$

where  $S_e$  = amount of contaminant adsorbed per unit weight of solid ( $\mu\text{g Kg}^{-1}$ )

$C_e$  = final concentration of contaminant in solution ( $\mu\text{g L}^{-1}$ )

$K_d$  = distribution coefficient ( $\text{L Kg}^{-1}$ ).

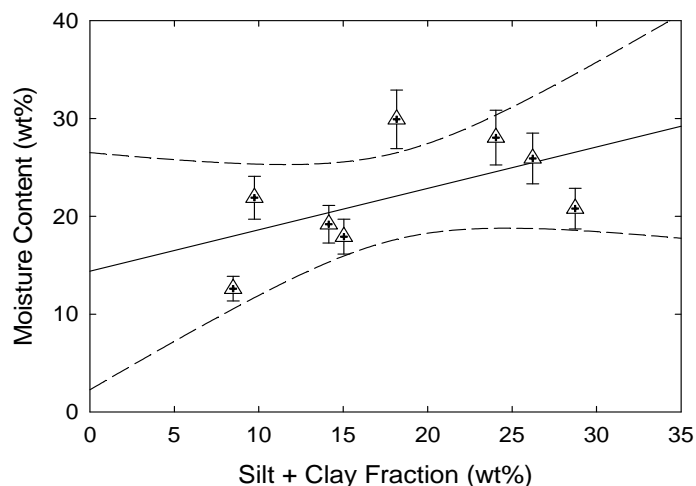
Linear regression analysis was conducted through zero, and  $K_d$  values were determined from Equation 2. The experimental uncertainties,  $2\sigma$ , were calculated using the estimated uncertainty of each measurement and the standard deviation between two measurements for each reported value.

## 5.0 Results and Discussion

### 5.1 Physical and Chemical Sediment Characteristics

#### 5.1.1 Moisture Content

All samples of this study were collected from the saturated zone and, therefore, are expected to have high moisture contents. Moisture contents averaged approximately 25 wt% (Table 5.1). A plot of gravimetric moisture content as a function of silt and clay content illustrates the relationship between these two parameters (Figure 5.1). With one exception, all values of moisture content fall within the 95% confidence interval (CI) relating an increase in moisture content to increase in silt and clay content. The upper Ringold unit sample B1JXB1 contained the lowest moisture content, which was attributed to the high gravel and sand content of this sample. Sediment sample B1D7M3 had apparently higher moisture content. This is attributed to the fine-grained texture of the sand comprising this sediment.



**Figure 5.1.** Graph Illustrating the Relationship between Moisture Content and wt% Silt and clay Fraction Comprising the Sediment at the 95% CI.

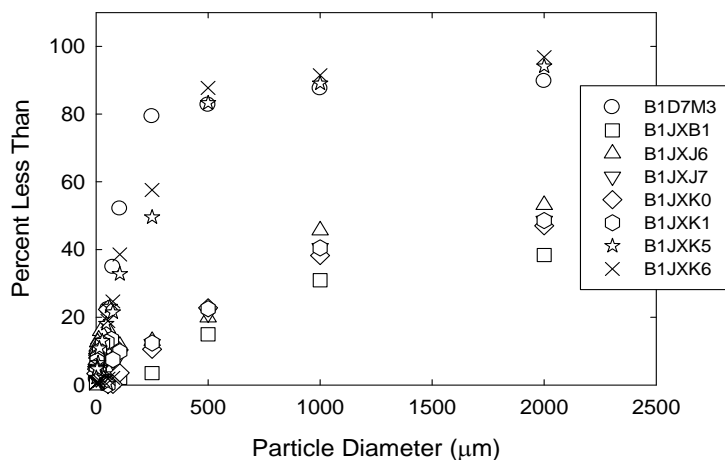
**Table 5.1.** Moisture Content of Sediments

Sediment	Lithology	Moisture Content (%)
B1D7M3	Ringold E: 5% gravel, 90% sand, 5% silt	29.91%
B1JXB1	Upper Ringold E: 40% sand, 5% silt, 55% gravel	12.60%
B1JXJ6	Ringold E gravel: 65% gravel, 20% sand, 15% silt and clay	20.78%
B1JXJ7	Ringold E gravel: 15% silt and clay, 45% sand, 40% gravel	17.92%
B1JXK0	Ringold E gravel: 50% sand, 30% gravel, 20% mud	19.18%
B1JXK1	Deeper Ringold gravel: 45% gravel, 35% mud, 20% sand	21.90%
B1JXK5	Deeper Ringold E gravel: 60% sand, 40% mud	28.04%
B1JXK6	Ringold Lower mud: 100% mud	25.91%



### 5.1.2 Particle Size and Density

Figure 5.2 depicts the particle-size distribution for sediment core samples. Samples B1D7M3, B1JXK5, and B1JXK6 had similar particle-size distribution, where > 80% of the total mass could be accounted for in the < 2 mm or lower size range. The remaining core samples—B1JXB1, B1JXJ6, B1JXJ7, B1JXK0, and B1JXK1—displayed a comparable size distribution with 40 to 60% of the mass in the 2-mm-and-lower particle-diameter range. A similar distribution profile behavior has been observed for other Hanford aquifer sediments (Riley et al. 2005).



**Figure 5.2.** Particle Size Distribution in Sediment Core < 2 mm Samples.

Particle size distributions of the selected sediment samples are presented in

Table 5.2. The < 2 mm sediments are predominantly a sand-silt mixture with minor clay fractions, up to approximately 10%. Most of the samples are gravel- and sand-dominated sediments, except B1JXK5 (Deep Ringold E) and B1JXK6 (Ringold Lower mud) collected from well 299-W14-72. Because of the fine-grained nature of the mud, fine-grained sand and silt were the dominant particle sizes in the samples.

The other samples are typical gravel- and sand-dominated Ringold Unit E formation, consistent with other geologic characterizations previously published (Bjornstad 1990; Connelly et al. 1992; Delaney et al. 1991; Fecht and Weekes 1996; Lindsey et al. 1994; Slate 2000; Williams et al. 2002; Wood et al. 2001).

**Table 5.2.** Particle-Size Distributions for Bulk Samples as Determined by Dry Sieve/Hydrometer Methods and Particle Density for < 2-mm Fraction as Determined by Pycnometry

Sediment	Gravel (%)	Sand (%)	Silt (%)	Clay (%)	Particle Density (< 2 mm) (g cm <sup>-3</sup> )
		< 2 mm Fraction			
B1D7M3	23.09	62.94	12.51	1.45	2.64
B1JXB1	65.46	31.61	2.72	0.21	2.66
B1JXJ6	74.52	18.16	17.19	0.13	3.87
B1JXJ7	69.92	30.93	3.81	0.79	2.62
B1JXK0	51.10	41.99	4.99	1.92	2.69
B1JXK1	74.62	22.91	0.96	1.51	2.61
B1JXK5	0.65	75.47	20.91	2.94	2.65
B1JXK6	0.53	73.39	17.54	8.54	2.66
<sup>†</sup> B19136 + B19137	42.0	52.2	4.34	1.46	<sup>*</sup> 2.65
<sup>†</sup> B19140	55.0	26.7	13.2	5.10	<sup>*</sup> 2.65

<sup>†</sup> B19377	0.0	20.8	69.3	9.83	<sup>*</sup> 2.65
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<sup>†</sup>Um et al., 2005

<sup>\*</sup>No direct particle-density measurements were made; assumed default value of 2.65 (Serne et al. 2004)

### 5.1.3 Specific Surface Area

Table 5.3 summarizes values of specific surface area for the different sediment-size fractions of ZP-1 core sediments used in this study, along with those previously investigated from the UP-1 operable unit. Bulk surface areas ranged from a low of 3.33 m<sup>2</sup> g<sup>-1</sup> to a high of 23.4 m<sup>2</sup> g<sup>-1</sup>. Surface areas of sediment-sand fractions were in the range of 0.26 m<sup>2</sup> g<sup>-1</sup> to 13.2 m<sup>2</sup> g<sup>-1</sup>. Surface areas for silt and clay fractions were in the range of 2.00 m<sup>2</sup> g<sup>-1</sup> to 14.82 m<sup>2</sup> g<sup>-1</sup>.

**Table 5.3.** Specific Surface Area of Different Sediment Size Fractions

Size Fraction	Bulk (< 2 mm) (m <sup>2</sup> g <sup>-1</sup> )	Sand Size (fine-to-medium) (0.125 < Size < 0.5 mm) (m <sup>2</sup> g <sup>-1</sup> )	Silt and Clay Size (< 0.05 mm) (m <sup>2</sup> g <sup>-1</sup> )
B1D7M3	9.77	3.93	4.59
B1JXB1	4.02	3.05	2.00
B1JXJ6	14.33	2.28	3.24
B1JXJ7	12.58	3.67	8.56
B1JXK0	5.57	2.58	25.06
B1JXK1	18.24	2.15	4.09
B1JXK5	11.24	0.26	14.82
B1JXK6	17.00	6.50	9.94
<sup>†</sup> B19136 + B19137	3.33	0.97	4.12
<sup>†</sup> B19140	23.4	13.2	23.3
<sup>†</sup> B19377	8.40	2.40	8.71

<sup>†</sup>Um et al. (2005)

### 5.1.4 Carbon Content

For those sediments containing measurable amounts of organic carbon, 200-ZP-1 sediments contained 0.02% to 0.04% organic carbon. Sediments from the previous study (200-UP-1) contained similar levels of organic carbon (Table 5.4). Comparable to one sample from the previous 200-UP-1 study (B19137), which contained 0.22% inorganic carbon (equivalent to 1.83% calcium carbonate), sediments B1JXJ7 and B1JXK0 contain 0.29% and 0.30% inorganic carbon, equivalent to 2.41% and 2.50% calcium carbonate respectively. Um et al. (2005) attributed the higher carbon content to the calcite content, originally present in these relatively old Ringold Unit sediments at their time of emplacement, being dissolved over the millennia by percolating groundwater, if the groundwater was unsaturated with respect to carbonate-bearing minerals. Moreover, today the 200-UP-1 groundwater within the Ringold Formation, based on geochemical modeling, is close to equilibrium with calcite and dolomite. Thus, either carbonates were removed in the past or the Ringold sediments may have been low in calcium carbonate content at the time of deposition.



**Table 5.4.** Total, Inorganic, and Organic Carbon Content for Core Sediment

Size Fraction	Total Carbon (%)	Inorganic Carbon (%)	Organic Carbon (%)
B1D7M3	<0.0199	<0.0269	0.00
B1JXB1	0.03	<0.0269	0.03
B1JXJ6	<0.0199	<0.0269	0.00
B1JXJ7	0.33	0.29	0.04
B1JXK0	0.34	0.30	0.04
B1JXK1	0.03	<0.0269	0.03
B1JXK5	<0.0199	<0.0269	0.00
B1JXK6	<0.0199	<0.0269	0.00
<sup>†</sup> B19136	0.03	<0.0269	0.03
<sup>†</sup> B19137	0.24	0.22	0.02
<sup>†</sup> B19140	0.04	<0.0269	0.04
<sup>†</sup> B19377	0.02	<0.0269	0.02

<sup>†</sup>Um et al. (2005)

## 5.2 CCl<sub>4</sub> Partition Coefficients

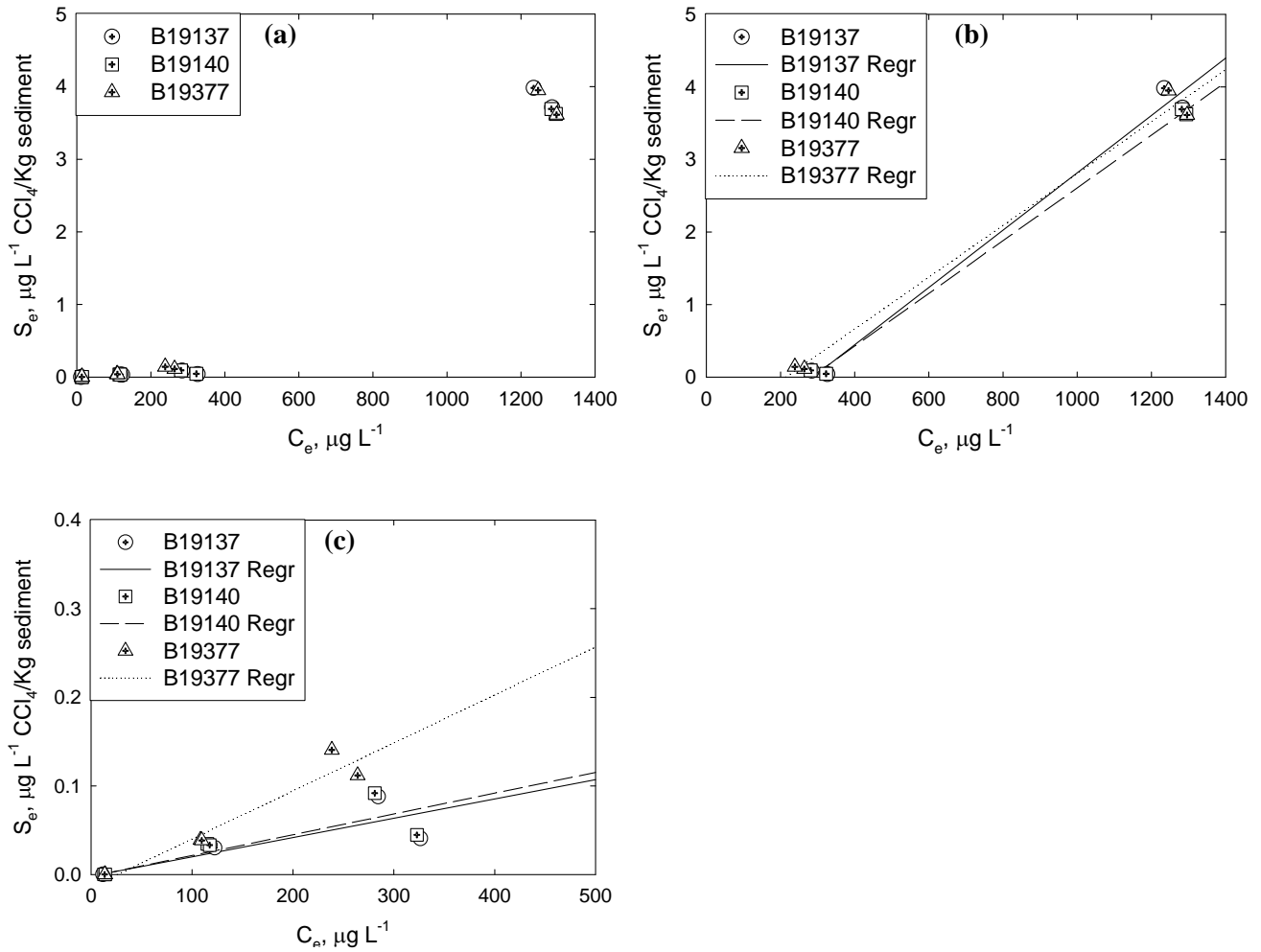
### 5.2.1 200-UP-1 Operable Unit Sediments

Sediment-free controls indicated that there was no loss of CCl<sub>4</sub> to the vials. The CCl<sub>4</sub>-free suspensions indicated that the C<sub>o</sub> solution was the only source of CCl<sub>4</sub>. The CCl<sub>4</sub> exhibited bimodal adsorption behavior over the concentration range, C<sub>o</sub>, (15 – 2500 µg L<sup>-1</sup>) for total CCl<sub>4</sub> in solution (Figure 5.3). The 95% confidence interval for the expected K<sub>d</sub> values was calculated using the lower and higher estimates for each of the sediments (shown in parentheses in Table 5.5). Duplicate concentrations were within analytical error, and the calculated distribution coefficients, K<sub>d</sub>, were within the 95% confidence interval.

**Table 5.5.** K<sub>d</sub> Values and Associated Ranges for 200-UP-1 Sediment Samples

Sediment	Fast (Phase 1) – Measured K <sub>d</sub> , L kg <sup>-1</sup>	Slow (Phase 2) – Measured K <sub>d</sub> , L kg <sup>-1</sup>
B19137	2.42 x 10 <sup>-4</sup> (1.52 x 10 <sup>-4</sup> – 3.32 x 10 <sup>-4</sup> )	2.89 x 10 <sup>-3</sup> (1.66 x 10 <sup>-3</sup> – 4.13 x 10 <sup>-3</sup> )
B19140	2.62 x 10 <sup>-4</sup> (1.56 x 10 <sup>-4</sup> – 3.69 x 10 <sup>-4</sup> )	2.70 x 10 <sup>-3</sup> (1.63 x 10 <sup>-3</sup> – 3.78 x 10 <sup>-3</sup> )
B19377	3.20 x 10 <sup>-4</sup> (1.93 x 10 <sup>-4</sup> – 4.47 x 10 <sup>-4</sup> )	2.88 x 10 <sup>-3</sup> (1.95 x 10 <sup>-3</sup> – 3.81 x 10 <sup>-3</sup> )

Plots of concentration of CCl<sub>4</sub> sorbed to sediment versus concentration in solution for the < 2 mm fraction of sediments B19137, B19140, and B19377 from the previous 200-UP-1 study are shown in Figure 5.3. Sorption of CCl<sub>4</sub> was linear over the concentration ranges, C<sub>e</sub>, of 15 to 400 µg L<sup>-1</sup> and 400 to 2500 µg L<sup>-1</sup>. All sediments displayed approximately the same degree of affinity for the sorption of CCl<sub>4</sub>. Organic carbon serves as the dominant sorbent for organic contaminants within sediment matrices. The organic carbon content of all three sediments was approximately equal, 0.02% – 0.04%, which is consistent with the low values of K<sub>d</sub> observed. However, initial adsorption of CCl<sub>4</sub> on sediment B19377, which is dominated by silt-sized particles, was two times greater than that measured for B19137 or B19140 (Table 5.5). It is hypothesized the high surface area of the silt particles within sediment B19377 affords rapid interaction with CCl<sub>4</sub>, resulting in an initial increase in adsorption relative to the sediments containing a higher portion of coarser particles. Sediment K<sub>d</sub> did not show any correlation with sediment surface area.



**Figure 5.3.** CCl<sub>4</sub> Isotherms for UP-1 Operable Unit Sediments. a) Adsorption of CCl<sub>4</sub> on sediments B19137, B19140, and B19377 over the concentration range 15 – 2500 µg L<sup>-1</sup>; b) isotherms for CCl<sub>4</sub> sorption over the concentration range of 400 – 2500 µg L<sup>-1</sup>; c) isotherms for CCl<sub>4</sub> sorption over the concentration range of 15 – 400 µg L<sup>-1</sup>.

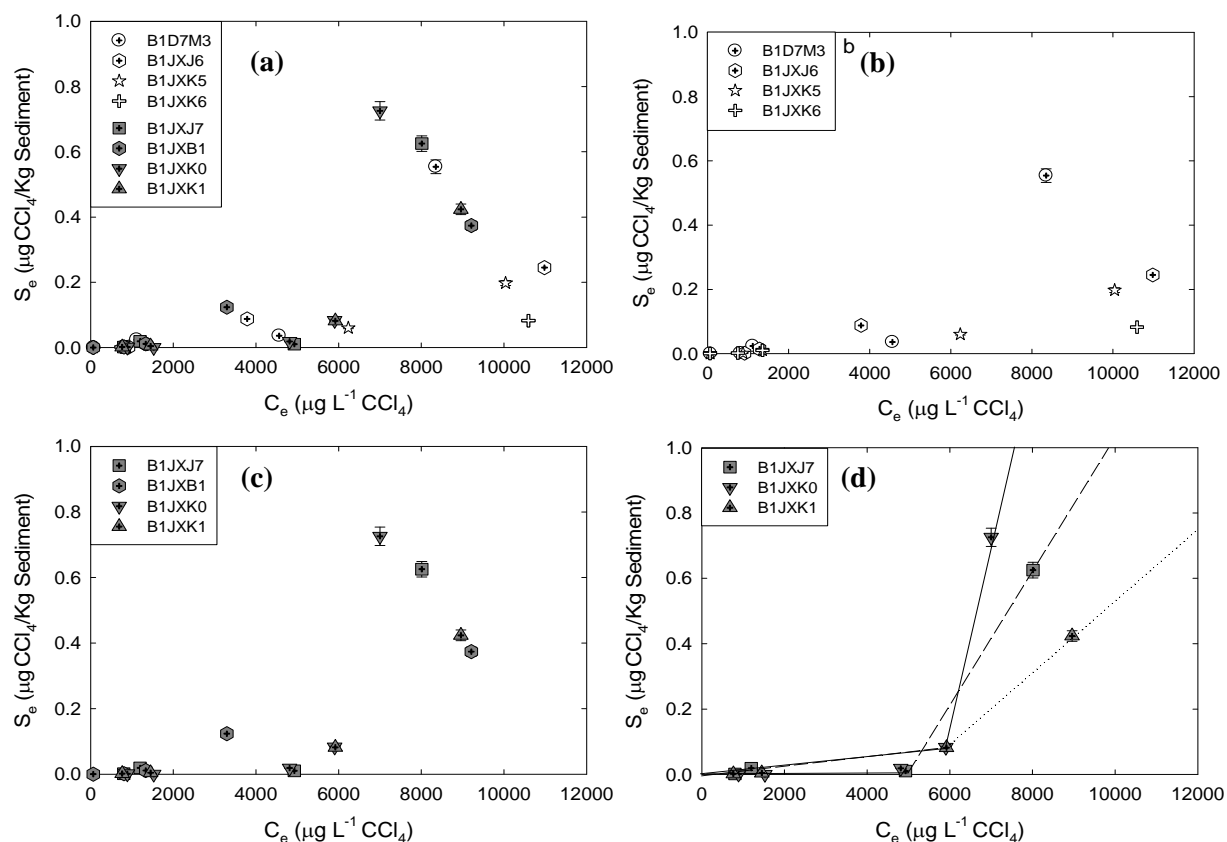
### 5.2.2 200-ZP-1 Operable Unit Sediments

Sediment-free controls indicated there was no loss of CCl<sub>4</sub> to the vials. The CCl<sub>4</sub>-free suspensions indicated that the C<sub>0</sub> solution was the only source of CCl<sub>4</sub>. The 95% confidence interval for the calculated *K<sub>d</sub>* values are shown in parentheses in Table 5.6.

**Table 5.6.**  $K_d$  Values and Associated Ranges for 200-ZP-1 Sediment Samples

Sediment	Fast (Phase 1) - Measured $K_d$ , L kg <sup>-1</sup>	Slow (Phase 2) - Measured $K_d$ , L kg <sup>-1</sup>
B1D7M3	$5.21 \times 10^{-5}$ ( $1.75 \times 10^{-5}$ – $8.68 \times 10^{-5}$ )	
B1JXJ7	$4.75 \times 10^{-5}$ ( $0.00$ – $9.50 \times 10^{-5}$ )	$2.44 \times 10^{-4}$ ( $0.00$ – $4.88 \times 10^{-4}$ )
B1JXJ6	$2.21 \times 10^{-5}$ ( $1.84 \times 10^{-5}$ – $2.59 \times 10^{-5}$ )	
B1JXB1	$4.00 \times 10^{-5}$ ( $3.39 \times 10^{-5}$ – $4.60 \times 10^{-5}$ )	
B1JXK0	$9.65 \times 10^{-6}$ ( $0.00$ – $1.93 \times 10^{-5}$ )	$3.14 \times 10^{-4}$ ( $0.00$ – $6.27 \times 10^{-4}$ )
B1JXK1	$1.31 \times 10^{-5}$ ( $4.57 \times 10^{-6}$ – $2.15 \times 10^{-5}$ )	$1.17 \times 10^{-4}$ ( $0.00$ – $2.33 \times 10^{-4}$ )
B1JXK5	$1.67 \times 10^{-5}$ ( $1.02 \times 10^{-5}$ – $2.32 \times 10^{-5}$ )	
B1JXK6	$7.76 \times 10^{-6}$ ( $7.09 \times 10^{-6}$ – $8.43 \times 10^{-6}$ )	

Plots of concentration of CCl<sub>4</sub> sorbed to sediment versus concentration in solution for the < 2 mm fraction of sediments are shown in Figure 5.4a. For CCl<sub>4</sub> concentrations < 6000 µg L<sup>-1</sup>, there were no apparent differences in CCl<sub>4</sub> sorption by the sediments (Figure 5.4a). However, sorption of CCl<sub>4</sub> was generally greater in sediments containing higher organic carbon contents in the presence of CCl<sub>4</sub> concentrations > 6000 µg L<sup>-1</sup> (Figure 5.4a-c). The noted exception to this is sediment B1D7M3, which displays comparable sorption of CCl<sub>4</sub> to sediments with ≥ 0.03% organic carbon. The reason for this seemingly anomalously high value is not evident based on measured physical and chemical properties of the sediments of this study. Sediment  $K_d$  did not show any correlation with sediment surface area.



**Figure 5.4.** CCl<sub>4</sub> Isotherms for ZP-1 Operable Unit Sediments. a) Adsorption of CCl<sub>4</sub> 200-ZP-1 sediments; b) isotherms for CCl<sub>4</sub> on 200-ZP-1 sediments containing ≤ 0.03% organic carbon content; c) isotherms for CCl<sub>4</sub> on 200-ZP-1 sediments containing ≥ 0.03%

organic carbon content; d) isotherms for  $\text{CCl}_4$  on 200-ZP-1 sediments containing  $\geq 0.03\%$  organic carbon content with guidelines indicating the bimodal behavior of  $\text{CCl}_4$  sorption.

## 6.0 Discussion

Sorption and desorption of organic contaminants by sediments is generally bimodal, in that it occurs via two stages—an initial fast sorption period occurring on the order of minutes to days (phase 1) and secondary slow sorption stage occurring over weeks to years (phase 2) (Luthy et al. 1997; Pignatello and Xing 1996). Sorption of CCl<sub>4</sub> to sediments from 200-UP-1 displayed an apparent bimodal behavior. Phase 1 behavior was represented by  $K_d$  values of  $2.42 \times 10^{-4}$  L kg<sup>-1</sup> to  $3.20 \times 10^{-4}$  L kg<sup>-1</sup>. Phase 2 behavior was represented by  $K_d$  values approximating  $3.00 \times 10^{-3}$  L kg<sup>-1</sup>; an order of magnitude greater than phase 1 values of  $K_d$ . Phase 1 adsorption of CCl<sub>4</sub> is suggestive of partitioning between the interfacial phase and the bulk solution without any specific bonding between the adsorbent and adsorbate (Sparks 1995). A conceptual model that would explain bimodal behavior is that the maximum concentration of CCl<sub>4</sub> rapidly saturated the limited number of adsorption sites associated with the organic carbon fraction. Subsequently, excess CCl<sub>4</sub>, coupled with a contact time of five days, allowed slower incorporation processes to occur (e.g., intraparticle diffusion), which can increase the apparent sorption distribution coefficient by 30% to 10-fold (Pignatello and Xing 1996).

The observed bimodal adsorption behavior of CCl<sub>4</sub> observed on 200-UP-1 sediments was also evident for sorption isotherms conducted on three of the eight 200-ZP-1 sediments - B1JXJ7, B1JXK0, and B1JXK1 (Figure 5.3b-c and Figure 5.4d). Phase 1  $K_d$  values measured for the eight 200-ZP-1 sediments ranged from  $9.65 \times 10^{-6}$  L kg<sup>-1</sup> to  $5.21 \times 10^{-5}$  L kg<sup>-1</sup>. For the three sediments exhibiting bimodal behavior, phase 2  $K_d$  values ranged from  $1.17 \times 10^{-4}$  L kg<sup>-1</sup> to  $3.14 \times 10^{-4}$  L kg<sup>-1</sup>. Analogous to the 200-UP-1 sediments, these three sediments from 200-ZP-1 contained 0.03% - 0.04% organic carbon content (Table 6.1). Although sediment B1JXB1 from 200-ZP-1 also contained 0.03% organic carbon, an apparent bimodal sorption behavior was not evident. Sediments from 200-ZP-1 and 200-UP-1, displaying bimodal sorption, also contained a silt and clay fraction with a surface area  $\geq 4$  m<sup>2</sup> g<sup>-1</sup>. Contrary to this, the surface area associated with the silt and clay fraction of B1JXB1 is 50% lower (Table 6.1). Thus, it is hypothesized a minimum silt and clay surface area and/or particle content, in combination with organic carbon, is necessary to observe bimodal sorption behavior of CCl<sub>4</sub> in short-contact batch tests.

Relative to  $K_d$  values quantified on 200-UP-1 sediment,  $K_d$  values measured for 200-ZP-1 sediments were approximately an order of magnitude less. It is possible the shorter contact time for 200-ZP-1 sediments limited the occurrence of slower sequestration processes (e.g., intraparticle diffusion), which can increase the apparent sorption-distribution coefficient by 30% to 10-fold (Pignatello and Xing 1996).

**Table 6.1.** Summary of 200-UP-1 and 200-ZP-1 Sediment Particle Distribution, Surface Area, Organic Carbon Content, and  $K_d$  Values

Sample	% Sand	% Silt and clay	Bulk SA (m <sup>2</sup> g <sup>-1</sup> )	SA (m <sup>2</sup> g <sup>-1</sup> ) Sand	SA (m <sup>2</sup> g <sup>-1</sup> ) Silt and clay	OC (%)	$K_d$ (L kg <sup>-1</sup> x 10 <sup>5</sup> )
B1JXJ6	71.3	28.7	14.33	2.28	3.24	0.00	2.2
B1JXK6	73.9	26.2	17.00	6.50	9.94	0.00	0.8
B1JXK5	76.0	24.1	11.24	0.26	14.82	0.00	1.7
B1D7M3	81.8	18.2	9.77	3.93	4.59	0.00	5.2
B1JXJ7	85.0	15.1	12.58	3.67	8.56	0.04	4.6
B1JXK0	85.9	14.1	5.57	2.58	25.06	0.04	1.0
B1JXK1	90.3	9.8	18.24	2.15	4.09	0.03	1.3
B1JXB1	91.5	8.5	4.02	3.05	2.00	0.03	4.0
B19377	20.8	79.1	8.40	2.4	8.71	0.02	32
B19140	59.3	40.7	23.4	13.2	23.3	0.04	26
B19136/B19137	90	10	3.33	0.97	4.12	0.02/0.03	24



## 7.0 Background, Context, and Perspective

Table 7.1 summarizes sources of CCl<sub>4</sub>  $K_d$  values and how they have been historically applied in models to assess the effects of CCl<sub>4</sub> source location and mass in the Hanford aquifer (Truex et al. 2001) and the transport and fate of CCl<sub>4</sub> in Hanford groundwater (Chiaramonte et al. 1996; Bergeron and Cole, 2004). Historically applied values have been estimated using organic carbon partition coefficients derived from soils with organic carbon contents similar to those of Hanford soils (Truex et al. 2001) or other sources (U.S. EPA 1995). Past assessments assumed complete advective transport of CCl<sub>4</sub> for some scenarios (i.e., a value of 0 L kg<sup>-1</sup> for  $K_d$  in selected scenarios) (Chiaramonte et al. 1996; Bergeron and Cole 2004) with other scenarios using estimated values of  $K_d$  in the range of 0.016 L/kg to 0.83 L kg<sup>-1</sup> (U.S. EPA, 1995; Chiaramonte et al. 1996; Bergeron and Cole, 2004; Truex et al. 2001). Past assessments tended to have in-common application of values in the range of 0.1 L kg<sup>-1</sup> to 0.3 L kg<sup>-1</sup>.

**Table 7.1.** Hanford Carbon Tetrachloride (CCl<sub>4</sub>)  $K_d$  Parameter Value Source and Application

CCl <sub>4</sub> $K_d$ Values	Source/Application
0 L kg <sup>-1</sup> , 0.114 L kg <sup>-1</sup> (Chiaramonte et al. 1996)	0.114L/kg literature estimate (U.S. EPA 1995). $K_d$ values applied within the VAM3DCG model to estimate CCl <sub>4</sub> groundwater migration at the Hanford site up to 200 years into the future, beginning in 1995.
0.016 L kg <sup>-1</sup> (minimum) 0.83 L kg <sup>-1</sup> (maximum) 0.12 L kg <sup>-1</sup> (most probable) (Truex et al. 2001)	$K_d$ values estimated from values of organic carbon partition coefficients ( $K_{oc}$ ) obtained from the literature for soils with organic carbon content similar to the organic carbon content of Hanford soils. Values applied within the Hanford Site-Wide Groundwater Model to assess CCl <sub>4</sub> source size on impact to a compliance boundary located 5,000 meters away.
0 L kg <sup>-1</sup> , 0.322 L kg <sup>-1</sup> (Bergeron and Cole 2004)	Median value of $K_d$ based on estimated $K_d$ values in Truex et al., 2001. Values applied within the Hanford Site-Wide Groundwater Model to estimate Hanford CCl <sub>4</sub> groundwater plume impacts to the Columbia River.
0.005 L kg <sup>-1</sup> , 0.165 L kg <sup>-1</sup> , 0.012 L kg <sup>-1</sup> (Cantrell et al. 2003)	Calculated values based on laboratory-batch sorption experiments with Hanford sediments from well 299-W11-27. Contact time of four days. Solution-to-solid ratio of 40:1.
0.144 L kg <sup>-1</sup> , 0.367 L kg <sup>-1</sup> (Riley et al. 2005)	Calculated values based on laboratory column desorption experiments with Hanford sediments from well 299-W15-46. Contact time up to 30 years.
0.00024 to 0.00032 L kg <sup>-1</sup> (Phase 1) 0.0027 to 0.0029 L kg <sup>-1</sup> (Phase 2) (Wellman et al. 2006, this study)	Calculated values based on laboratory-batch sorption experiments with Hanford sediments from wells 699-36-70B and 299-W19-48. Contact time of five days. Solution-to-solid ratio of 100:1.
0.00000776 to 0.0000521 L kg <sup>-1</sup> (This study)	Calculated values based on laboratory-batch sorption experiments with Hanford sediments from wells 299-W11-43, 299-W11-86, 299-W14-71, and 299-W14-72. Contact time of three days. Solution-to-solid ratio of 100:1.

Experimentally derived values of CCl<sub>4</sub>-sorption  $K_d$  have been obtained with Hanford soils and sediments. The  $K_d$  values in the range of 0.005 L kg<sup>-1</sup> to 0.165 L kg<sup>-1</sup> were obtained from sediments collected from Hanford 200 West Area, well 299-W11-27. Experimentally derived values of CCl<sub>4</sub>  $K_d$  presented in this report for aquifer sediments collected from 200 UP-1 and 200-ZP-1 are lower than those experimentally determined or applied to past assessments. Differences are attributed to higher organic carbon contents assigned to Hanford assessments and subsequent higher  $K_d$  values assigned to those

sediments. The short-contact times of the experiments described in this study also likely contributed to the low  $K_d$  values observed. The influence of contact time on  $K_d$  can be seen in the values of  $\text{CCl}_4$   $K_d$  derived from column-desorption experiments performed on Hanford aquifer sediments that had been in contact with  $\text{CCl}_4$  for 30 years (Riley et al. 2005).  $K_d$  values determined in the desorption study were roughly three to four orders of magnitude higher than those described in this study. These data are scientifically defensible alternatives for application in future Hanford assessments. This includes an alternative to the most conservative assumption of complete advective transport of  $\text{CCl}_4$  in Hanford groundwater (i.e., application of a 0 L/kg value of  $K_d$ ). A most recent application of the experimentally derived desorption  $K_d$  values (Riley et al. 2005) was to the estimation of  $\text{CCl}_4$  inventory in 200 West Area's unconfined aquifer (Murray et al. 2006).



## 8.0 Conclusions

The 200-UP-1 sediments of this study had measurable organic carbon contents of 0.02% to 0.04%, typical of Hanford aquifer sediments. The organic carbon content of some of the 200-ZP-1 sediments was below the level of detection.  $\text{CCl}_4$   $K_d$  values were determined on aquifer sediments from the 200-UP-1 and 200-ZP-1 operable units located in the Hanford site's 200 West Area.  $\text{CCl}_4$   $K_d$  values for 200-UP-1 sediments ranged from 2.42 to  $3.20 \times 10^{-4}$  L kg<sup>-1</sup>. The  $\text{CCl}_4$   $K_d$  values for 200-ZP-1 sediments ranged from 0.96 to  $5.21 \times 10^{-5}$  L kg<sup>-1</sup>. The degree of sorption is frequently correlated with the organic carbon content and fine-textured fraction (e.g. silt or clay fraction) of sedimentary matrices, which contains the highest percentage of reactive surface sites. Bimodal sorption behavior of  $\text{CCl}_4$  in this investigation correlated with organic content but not with bulk or fraction-specific sediment surface area. Values of  $\text{CCl}_4$   $K_d$  for 200-UP-1 sediments were an order of magnitude higher than those observed for 200-ZP-1 sediments, even though the organic carbon content of the sediments compared were similar. It is possible the shorter contact time for 200-ZP-1 sediments limited the occurrence of slower sequestration processes (e.g., intraparticle diffusion). Alternatively, the difference may be attributed in part to the higher silt and clay contents of the 200-UP-1 sediments. These data contribute to a larger  $K_d$  database associated with Hanford sediments. The experimentally derived  $K_d$  values of this study are defensible alternatives to the most conservative assumption of complete advective transport of  $\text{CCl}_4$  in Hanford groundwater (i.e., application of a 0 L/kg value of  $K_d$ ) for application in future Hanford assessments.



## 9.0 References

- ASTM. 2001. *Standard Test Method for Determining a Sorption Constant ( $K_{oc}$ ) for an Organic Chemical in Soil and Sediment*, E1195-01, ASTM International, West Conshohocken, PA.
- ASTM. 2002. *Standard Test Method for Particle-Size Analysis of Soils*, D422-63, ASTM International, West Conshohocken, PA.
- ASTM. 2004. *Standard Test Method for 24-Hour Batch-Type Measurement of Volatile Organic Sorption by Soils and Sediments*, D5285-03, ASTM International, West Conshohocken, PA.
- Bergeron, MP, and CR Cole. 2004. *Recent Site-Wide Transport Modeling Related to the Carbon Tetrachloride Plume at the Hanford Site*, PNNL-14855, Pacific Northwest National Laboratory, Richland, Washington.
- Bjornstad BN. 1990. *Geohydrology of the 218-W-5 Burial Ground*, PNL-7336, Pacific Northwest Laboratory, Richland, Washington.
- Brunauer S, PH Emmett, and E Teller. 1938. "Adsorption of Gases in Multimolecular Layers." *Journal of the American Chemical Society* **60**:300-319.
- Cantrell, KJ, RJ Serne, and GV Last. 2003. *Hanford Contaminant Distribution Coefficient Database and Users Guide*, PNNL-13895, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.
- Chiaromonte, GR, CW Denslow, AJ Knepp, RD Langdon, and S Panday. 1996. *Hanford Site-Wide Groundwater Remediation Strategy-Groundwater Contaminant Predictions*, BHI-00469, Rev. 1., Bechtel Hanford, Inc., Richland, Washington.
- Connelly MP, BH Ford, and JV Borghese. 1992. *Hydrogeologic Model for the 200 West Groundwater Aggregate Area*, WHC-SD-EN-TI-014, Westinghouse Hanford Company, Richland, Washington.
- Delaney CD, KA Lindsey, and SP Reidel. 1991. *Geology and Hydrology of the Hanford Site: A Standardized Text for Use in Westinghouse Hanford Company Documents and Reports*, WHC-SC-ER-TI-003, Westinghouse Hanford Company, Richland, Washington.
- Fecht KR, and DC Weekes. 1996. *Geologic Field Inspection of the Sedimentary Sequence at the Environmental Restoration Disposal Facility*, BHI-00230, Bechtel Hanford, Inc., Richland, Washington.
- Hartman, MJ, LF Morasch, and WD Webber. 2007. *Summary of Hanford Site Groundwater Monitoring for Fiscal Year 2006*. PNNL-16342-SUM, Pacific Northwest National Laboratory, Richland, Washington.
- Murray, C, Yi-Ju Chien and M Truex. 2006. *Geostatistical Analysis of the Inventory of Carbon Tetrachloride in the Unconfined Aquifer in the 200 West Area of the Hanford Site*. Letter Report prepared by Pacific Northwest National Laboratory for Fluor Hanford, Richland, Washington, January 4, 2006.
- Riley, RG, JE Szecsody, DS Sklarew, AV Mitroshkov, CF Brown, CJ Thompson, and PM Gent. 2005. *Carbon Tetrachloride and Chloroform Partition Coefficients Derived from Aqueous Desorption of*

*Contaminated Hanford Sediments*, PNNL-15239, Pacific Northwest National Laboratory, Richland, Washington.

Serne RJ, BN Bjornstad, DG Horton, DC Lanigan, CW Lindenmeier, MJ Lindberg, RE Clayton, VL LeGore, RD Orr, SR Baum, KN Geiszler, MM Valenta, and TS Vickerman. 2004. *Characterization of Vadose Zone Sediments Below the Tx Tank Farm: Boreholes C3830, C3831, C3832 and Rcra Borehole 299-W10-27*, PNNL-14849, Pacific Northwest National Laboratory, Richland.

Sing KSW, DH Everett, RAW Haul, L Moscou, RA Pierotti, J Rouquerol, and T Siemieniewska. 1985. "Reporting Physisorption Data for Gas/Solid Systems with Special Reference to the Determination of Surface Area and Porosity." *Pure and Applied Chemistry* **57**(4):603 – 619.

Slate JL. 2000. *Nature and Variability of the Plio-Pleistocene Unit in the 200 West Area of the Hanford Site*, BHI-01203, Rev. 0, Bechtel Hanford, Inc., Richland, Washington.

Truex, MJ, CJ Murray, CR Cole, RJ Cameron, MD Johnson, RS Skeen, and CD Johnson. 2001. *Assessment of Carbon Tetrachloride Groundwater Transport in Support of the Hanford Carbon Tetrachloride Innovative Technology Demonstration Program*, PNNL-13560, Pacific Northwest National Laboratory, Richland, Washington.

Um W, RJ Serne, BN Bjornstad, HT Schaef, CF Brown, VL LeGore, KN Geiszler, SR Baum, MM Valenta, IV Kutnyakov, TS Vickerman, and MJ Lindberg. 2005. *Characterization of 200-up-1 Aquifer Sediments and Results of Sorption-Desorption Tests Using Spiked Uncontaminated Groundwater*, PNNL-15502, Pacific Northwest National Laboratory, Richland, WA.

U.S. EPA. 1995. *Background Document for EPACMTP: Finite Methodology for Degrading Chemicals with Transformation Products*, U.S Environmental Protection Agency, Office of Solid Waste, Washington, D.C.

Wellman, DM, RG Riley, KE Parker, and AV Mitroshkov. 2006. *Adsorption of Carbon tetrachloride to Sediments from the UP-1 Operable Unit*, PNNL-16100, Pacific Northwest National Laboratory, Richland, Washington.

Williams BA, BN Bjornstad, R Schalla, and WD Webber. 2002. *Revised Hydrogeology for the Suprabasalt Aquifer System, 200 West Area and Vicinity, Hanford Site, Washington*, PNNL-13858, Pacific Northwest National Laboratory, Richland, Washington.

Wood MI, R Schalla, BN Bjornstad, and FN Hodges. 2001. *Subsurface Conditions Description of the T and Tx-Ty Waste Management Areas*, RPP-7123, Rev. 0, CH2MHill Hanford Group, Inc., Richland, Washington

Riley, RG, and JM Zachara. 1992. *Chemical Contaminants on DOE Lands and Selection of Contaminant Mixtures for Subsurface Science Research*. DOE/ER-0547T, U.S. Department of Energy, Office of Energy Research, Subsurface Science Program, Washington, DC.

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