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Adsorption of Carbon Tetrachloride to Sediments from the UP-1 Operable Unit

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September 2006

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



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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 (C4298, C4299, and C4300) were sent to Pacific Northwest National Laboratory for characterization and quantification of contaminant retardation. These cores were 4-inches in diameter by 6-inches in length and were taken from depths near the unconfined aquifer surface (water table) to locations approximately 150 to 180 ft below the water table.

Prior to this work, no 200-UP-1 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 operable unit groundwater plume. Site-specific sorption data for carbon tetrachloride (CCl_4) was obtained with the <2 mm size fractions of uncontaminated 200-UP-1 sediments taken from two of these boreholes (C4299 and C4300) and distribution coefficients determined. Each fraction exhibited bimodal CCl_4 adsorption isotherms over the concentration range (15 – 2500 $\mu\text{g L}^{-1}$) for total CCl_4 in solution. Sorption of CCl_4 was linear over the concentration ranges of 15 to 400 $\mu\text{g L}^{-1}$ and 400 to 2500 $\mu\text{g L}^{-1}$.

The K_d values measured for the three 200-UP-1 sediments exhibited bimodal sorption with initial K_d values ranging from 0.0002 to 0.0005, and phase 2 values approximately 0.003 for all sediments. The measure K_d values are lower than the range calculated for CCl_4 in a Hanford soil (0.016 to 0.83 L/Kg) containing an average organic carbon content of 0.2% (Truex et al., 2001). The best estimate value of Truex et al. (2001) is 0.06 L/Kg based on a 0.1% sediment organic carbon content. However, this estimate is based on an organic carbon content up to an order of magnitude greater than the organic carbon content of the sediments tested herein. Prolonged contact may increase adsorption of CCl_4 as a result of mineral driven sorption and intraparticle diffusion.

K_d values obtained on sediment samples from 200-UP-1 contributes to a larger K_d database that exists for other Hanford sediments, and contains significant desorption data for CCl_4 . Comparison of previous data with new results (e.g., from this study) will allow inferences to be made on how the 200-UP-1 K_d values for CCl_4 may compare with sediments from other Hanford locations. Adsorption results presented here validate the use of a linear adsorption isotherm (K_d) to predict short contact time CCl_4 adsorption to sediments in 200-UP-1 groundwater plume for a distinct ranges in CCl_4 concentration. However, this does not imply that values of K_d will be constant if the groundwater chemical composition at 200-UP-1 changes with space or time. This site-specific sorption data, when complemented by the chemical, geologic, mineralogic, hydrologic, and physical characterization data that are also being collected (see *Sampling and Analysis Plan for the 200-UP-1 Groundwater Monitoring Well Network*, DOE 2002) can be used to develop a robust, scientifically defensible data base to allow risk predictions to be generated and to aid in future remediation decisions for the 200-UP-1 operable unit.

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Acronyms

200-UP-1	Groundwater Operable Unit in 200 W
BET	Brunauer-Emmett and Teller Nitrogen Adsorption
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
FHI	Fluor Hanford, Inc.
GC-MS	Gas Chromatography-Mass Spectrometry
K_d	Distribution Coefficient
S_e	Contaminant Concentration on Solid Phase

1.0 Introduction

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 from three of the wells, C4298, C4299, and C4300 were sent to Pacific Northwest National Laboratory for characterization and quantification of contaminant retardation. These cores were 4-inches in diameter by 6-inches in length and were taken from depths near the unconfined aquifer surface (water table) to locations approximately 150 to 180 ft below the water table.

Prior to this work, no 200-UP-1 site-specific adsorption data (i.e., K_d values) were available for the sediments or key contaminants present in the 200-UP-1 operable unit groundwater plume. Site-specific sorption data for carbon tetrachloride (CCl_4) was obtained with the uncontaminated sediment from two of these boreholes, C4299 and C4300. K_d values obtained on the sediment samples contributes to a larger K_d database for other Hanford sediments, which contains significant adsorption and desorption data for CCl_4 . Comparison of previous data with new results will allow inferences to be made on how the 200-UP-1 K_d values for contaminants of concern (COCs) may compare with sediments from other Hanford locations. This site-specific sorption data, when complemented by the chemical, geologic, mineralogic, hydrologic, and physical characterization data that are also being collected (see *Sampling and Analysis Plan for the 200-UP-1 Groundwater Monitoring Well Network*, DOE 2002) can be used to develop a robust, scientifically defensible data base to allow risk predictions to be generated and to aid in future remediation decisions for the 200-UP-1 operable unit.

2.0 Materials and Methods

2.1 Determination of Distribution Coefficient

Distribution coefficients (K_d) were determined in batch experiments for 3 sediment samples, designated B19137, B19140, and B19377, collected from the UP-1 Operable Unit. Note that sediment B19137 is a composite sample of B19136 and B19137. The K_d (mL/g), defined as:

$$K_d = \frac{\text{concentration of contaminant on the sediment}}{\text{concentration of contaminant in solution}} \quad (1)$$

K_d 's were determined from measurement of CCl_4 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_e were due to sorption of CCl_4 to the sediments. The American Society of Testing Materials, ASTM D 4319-93, (2001) standard test methodology was used for determining K_d values. For all batch experiments, the solution to solid ratio utilized was 1:100 with a five day contact time.

Five different initial concentrations, C_o ($\mu\text{g L}^{-1}$), of CCl_4 that range from 5 to 3000 $\mu\text{g L}^{-1}$ were added to batch experiment sediment samples. This concentration range included the Environmental Protection Agency Maximum Contaminant Level for CCl_4 (5 $\mu\text{g L}^{-1}$) and higher levels historically observed in the Hanford CCl_4 groundwater plume. Batch experiments were run in duplicate and included control samples that were free of either sediment or CCl_4 .

2.2 Analysis of Aqueous Samples by Gas Chromatography-Mass Spectrometry

The GC-MS was conducted according to standard technical procedures developed by the Pacific Northwest National Laboratory (PNNL). The water samples were diluted 4-500 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 502.2 Calibration Mix #2).

2.3 Data Analysis

Data from the adsorption experiments were fit with linear, or C-curve, adsorption isotherms. The linear equation has the form:

$$S_e = K_d C_e \quad (2)$$

where S_e is the amount of contaminant adsorbed per unit weight of solid (mol/g), C_e is the final concentration of contaminant in solution, and K_d is the distribution coefficient (Sparks, 1995; Sposito, 1989). Linear regression analysis was conducted through zero and K_d values were determined from the equation 2. The experimental uncertainties, 2σ , were calculated from the

estimated uncertainty of each measurement and the standard deviation between two measurements for each reported value.

3.0 Results and Discussion

3.1 Sediment Sample Characteristics

The < 2 mm fraction of three sediment samples, designated B19137, B19140, and B19377, collected from the UP-1 Operable Unit, were evaluated for retention of CCl₄. Sediment B19137 consists of a homogenized composite sample of sediment B19136 and B19137. Physical and chemical properties of the sediments were previously quantified by Um et al. (2005). Properties relevant to the retention of CCl₄ including, organic and inorganic carbon content, bulk fraction distribution, particle size distribution, and surface area are summarized below (Tables 1 – 3) (Um et al., 2005).

The three sediments bracket the particle size distribution from sand dominated (B19136 + B19137), sand-silt mixture (B19140), and silt dominated (B19377) (Table 1). Table 2 presents the measurements of specific surface area for the different size fractions for the three sediments. The highest surface area was observed in B19140 sediment, a sand-silt mixture, and was also observed in the sand-sized fraction of B19140. This was attributed to the presence of porous iron oxide coating around the surfaces of the particles (Um et al., 2005). The organic carbon content within the three sediments was determined by the difference between the inorganic carbon and total carbon concentration. All sediments contained comparable amounts of organic carbon 0.02 – 0.05% (Table 3).

Table 1. Summary of Particle-Size Distributions for Bulk Samples as Determined by Dry Sieve/Hydrometer Methods

Sediment	Gravel (%)	Sand (%)	Silt (%)	Clay (%)
		<2mm Fraction		
B19136 + B19137	42.0	52.2	4.34	1.46
B19140	55.0	26.7	13.2	5.10
B19377	0.0	20.8	69.3	9.83

Table 2. Specific Surface Area of Different Size Fractions from 200-UP-1 Sediments

Size Fraction	B19136 + B19137 (m ² /g)	B19140 (m ² /g)	B19377 (m ² /g)
Bulk (< 2 mm)	3.33	23.4	8.40
Sand Size (fine to medium) (0.125 < Size < 0.5 mm)	0.97	13.2	2.40
Silt and Clay Size (< 0.05 mm)	4.12	23.3	8.71

Table 3. Carbon Content of Sediments, and pH, Alkalinity, and EC of 1:1 Water Extracts

Sediment	Well	Total Carbon (%)	Inorganic Carbon (%)	Organic Carbon (%)	Alkalinity (mg/L)	pH	EC (mS/cm)
B19136	C4299	0.03	0.00	0.03	743.4 (108.3)	7.59 (7.81)	1.812 (0.318)
B19137	C4299	0.24	0.22	0.02	577.9 (60.0)	7.58 (7.45)	0.961 (0.214)
B19140	C4299	0.04	0.00	0.04	170.2 (ND)	7.48 (ND)	0.573 (ND)
B19377	C4300	0.02	0.00	0.02	178.7 (99.6)	7.59 (7.67)	0.400 (0.237)

3.2 CCl₄ Distribution Coefficients

Plots of concentration of CCl₄ sorbed to sediment versus concentration in solution for the < 2 mm fraction of sediments B19137, B19140, and B19377 are shown in Figure 1. Sediment-free controls indicated that there was no loss of CCl₄ to the vials. The CCl₄-free suspensions indicated that the C_o solution was the only source of CCl₄. CCl₄ exhibited bimodal adsorption behavior over the concentration range, C_o, (15 – 2500 µg L⁻¹) for total CCl₄ in solution (Figure 1). Sorption of CCl₄ was linear over the concentration ranges, C_e, of 15 to 400 µg L⁻¹ and 400 to 2500 µg L⁻¹. 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 and secondary slow sorption stage occurring over weeks to years (Luthy et al., 1997; Pignatello and Xing, 1996).

The 95% confidence interval, CI, for the expected K_d values were calculated using the lower and higher estimates for each of the sediments (shown in parentheses in Table 4). Duplicate concentrations were within analytical error and the calculated distribution coefficients, K_d , were within the 95% confidence interval.

Comparison of K_d values calculated for initial rapid adsorption (phase 1) with values calculated for the slower sorption (phase 2) of CCl₄ indicates all three sediments display K_d values of ~0.0003 L/kg for phase 1; whereas, K_d values calculated for phase 2 sorption are an order of magnitude greater, ~0.003 L/kg. Phase 1 adsorption of CCl₄ is indicative of partitioning between the interfacial phase and the bulk solution without any specific bonding between the adsorbent and adsorbate (Sparks, 1995). It is hypothesized the maximum concentration of CCl₄ utilized in this investigation rapidly saturated the limited number of adsorption sites associated with the organic carbon fraction. Subsequently, excess CCl₄, coupled with a contact time of five days, allow 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).

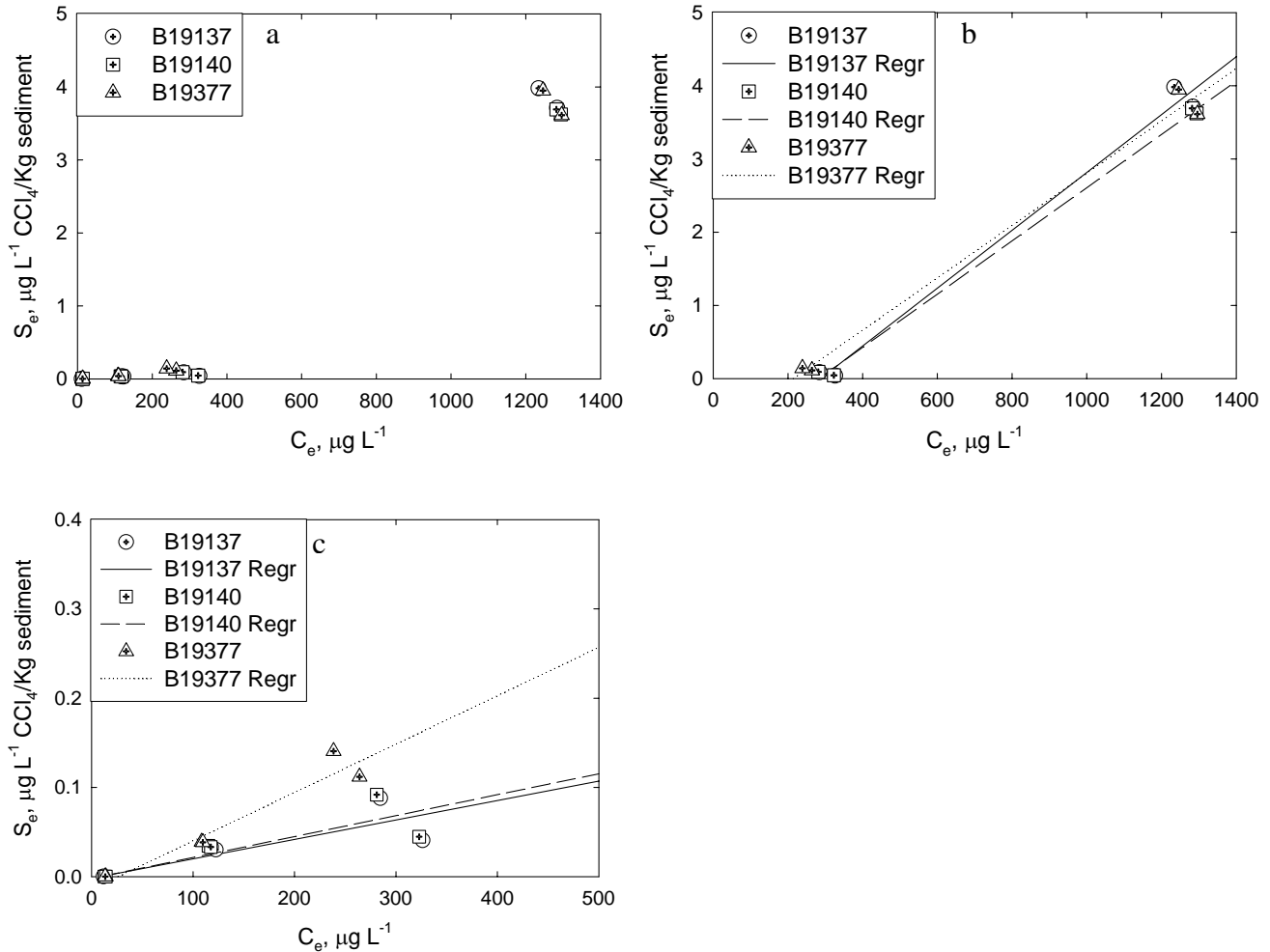


Figure 1. CCl_4 Isotherms for UP-1 Operable Unit Sediments. a) Adsorption of CCl_4 on sediments B19137, B19140, and B19377 over the concentration range $15 - 2500 \mu\text{g L}^{-1}$, b) isotherms for CCl_4 sorption over the concentration range of $400 - 2500 \mu\text{g L}^{-1}$, c) isotherms for CCl_4 sorption over the concentration range of $15 - 400 \mu\text{g L}^{-1}$.

All sediments displayed approximately the same degree of affinity for the sorption of CCl_4 . Organic carbon serves as the dominant sorbent for organic contaminants within sediment matrices. The organic carbon content of all three sediments was approximately equal, $0.02 - 0.05\%$, which is consistent with the similarity in magnitude and low values of K_d observed. However, initial adsorption of CCl_4 on sediment B19377, which is dominated by silt sized particles, was 2x greater than that measured for B19137 or B19140 (Table 4). It is believed the high surface area of the silt particles within sediment B19377 affords rapid interaction with CCl_4 resulting in an initial increase in adsorption relative to the sediments containing a higher portion of coarser particles.

Table 4. K_d Values and Associated Ranges for 200-UP-1 Sediment Samples

Sediment	Phase 1 - Measured K_d , L/kg	Phase 2 - Measured K_d , L/kg
B19137	0.00021 (0.00013 – 0.00029)	0.0029 (0.0017 – 0.0041)
B19140	0.00023 (0.00014 – 0.00031)	0.0027 (0.0016 – 0.0038)
B19377	0.00047 (0.00046 – 0.00057)	0.0029 (0.0019 – 0.0038)

The K_d values measured for the three 200-UP-1 sediments are lower than the range of K_d values calculated for CCl_4 in a Hanford soil containing an average organic carbon content of 0.2%, 0.016 to 0.83 L/Kg (Truex et al., 2001). The best estimate value of Truex et al. (2001) is 0.06 L/Kg based on a 0.1% sediment organic carbon content. However, this estimate is based on an organic carbon content one order of magnitude greater than the organic carbon content of the sediments tested herein. Additionally, distribution coefficients previously determined from desorption experiments utilizing aquifer sediments that had been in contact with CCl_4 for decades also afford higher K_d values (Riley et al., 2005). Prolonged contact allows significant mineral driven sorption and intraparticle diffusion. As such, the apparent desorption rate measured via aqueous desorption testing will be dominated by the increased retention afforded through these processes. Given a longer contact time for laboratory batch tests, small differences in the sorption of carbon tetrachloride and further increases in adsorption of carbon tetrachloride may be observed based on variations in mineral driven sorption and intraparticle diffusion I find this sentence confusing.

K_d values obtained on sediment samples from 200-UP-1 contributes to a larger K_d database that exists for other Hanford sediments, and contains significant desorption data for CCl_4 . Comparison of previous data with new results (e.g., from this study) will allow inferences to be made on how the 200-UP-1 K_d values for CCl_4 may compare with sediments from other Hanford locations. Adsorption results presented here validate the use of a linear adsorption isotherm (K_d) to predict short contact time CCl_4 adsorption to sediments in 200-UP-1 groundwater plume for a distinct ranges in CCl_4 concentration. However, this does not imply that values of K_d will be constant if the groundwater chemical composition at 200-UP-1 changes with space or time. This site-specific sorption data, when complemented by the chemical, geologic, mineralogic, hydrologic, and physical characterization data that are also being collected (see *Sampling and Analysis Plan for the 200-UP-1 Groundwater Monitoring Well Network*, DOE 2002) can be used to develop a robust, scientifically defensible data base to allow risk predictions to be generated and to aid in future remediation decisions for the 200-UP-1 operable unit.

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