Kelsey Winsor is from Rhode Island and went to Smith College in Massachusetts, where she majored in geology and minored in philosophy. Through SULI, she interned at the Pacific Northwest National Laboratory in the spring of 2007, and worked there as a research associate during the following year. She plans to attend grad school to study ocean-climate interactions, and hopes to apply her research to identifying causes of regional changes in water resources and ecology. Outside of science, she likes to backpack and is trying to learn kung fu.

George V. Last is a senior research scientist at the Pacific Northwest National Laboratory. He received his B.S. degree in Geology and M.S degree in Environmental Science (Hydrogeology Option) from Washington State University. He is a registered professional geologist and hydrogeologist in the states of Washington and Oregon. Throughout his 32 year career, his research has focused on applied subsurface science aimed at improving our understanding of the geologic controls on contaminant fate and transport and methodologies for predicting the spatial distribution of hydrologic and geochemical properties.

Stratigraphic Control on CCl_4 and $CHCl_3$ Concentrations in the 200 West Area, Hanford Site

Kelsey Winsor and George V. Last

ABSTRACT

An extensive subsurface contaminant plume of carbon tetrachloride (CCl_4) is the focus of a remedial effort in the 200 West Area of the U.S. Department of Energy's Hanford Site in eastern Washington. Remediation requires a high-resolution understanding of the region's spatially variable lithofacies and of the effect these lithofacies have on CCl_4 migration through the unconfined aquifer. To increase the level of detail of our current understanding, a transect was chosen along the primary groundwater flow path in the most heavily contaminated area. Borehole logs of wells along this 3.7 km-long transect were standardized and used to create a cross section displaying the depth and continuity of lithofacies. Natural and spectral gamma geophysical logs were examined to pinpoint the depths of geologic units. Depth discrete concentrations of CCl_4 and its reductive dechlorination product, chloroform ($CHCl_3$), were overlain on this cross section. Comparison of stratigraphy to contaminant levels shows that peaks in CCl_4 concentration occur in thin, fine-grained layers and that other fine-grained layers frequently form lower boundaries to regions of high concentration. Peaks in CCl_4 concentrations are frequently located at different depths from those of $CHCl_3$, suggesting that these concentrations are affected by dechlorination of CCl_4. Transformation of CCl_4 to $CHCl_3$ appears to be more prevalent within reduced, iron-containing sediments. The influence of thin, fine-grained layers within the larger aquifer unit indicates that characterization of contamination in this locality should consider subsurface geology with at least as much resolution as provided in this study.

Introduction

Enormous volumes of waste water, which included a range of chemical and radioactive contaminants, have been disposed in the 200 West Area of the U.S. Department of Energy's Hanford Site in eastern Washington [1]. Without complete natural attenuation and/or remediation, contaminants reaching the groundwater will eventually enter the Columbia River [2, 1]. The river is vital to regional salmon and is an important water resource for human developments in the Pacific Northwest. Of particular interest to this study is tetrachloromethane, or carbon tetrachloride (CCl_4). This liquid was used during the plutonium finishing process between 1955 and 1973, and 750,000 kg of CCl_4 was disposed of in cribs and trenches in the 200 West Area [3]. Subsequent drainage through the thick vadose zone has released an estimated 132,000 kg of this contaminant into the unconfined aquifer, creating a large groundwater plume [4, 5]. Found in concentrations above the drinking water standard (5 µg/L) over an area of 10.78 km^2, the CCl_4 plume has spread significantly in the past 15 years and several remediation treatments are being conducted to restrict the plume [6]. Background levels of CCl4 in Hanford Site sediments are below the 5 µg/L drinking standard [6].

Subsurface geology and groundwater flow are the primary determinants of contaminant migration in this arid region [7]. While the Hanford Site's geology has been studied extensively [8, 1], uncertainties remain regarding variation in depths and extent of sedimentary units below the site. Stratigraphic complexity is greatly influenced by spatially variable fluvial and flood deposits and erosional features. General stratigraphy in the 200 West Area includes some 160 m of fluvial, lacustrine, and eolian deposits above basalt bedrock. The lowermost formation, the Ringold, is a fluvial/lacustrine deposit and locally consists of three major units; sands and gravels (Ringold A), overlain by an impermeable but discontinuous mud and sand (Ringold Lower Mud), overlain in turn by a thick sequence of sands and gravels (Ringold E). Both confined and unconfined aquifers are located in the Ringold

Formation. Groundwater in the Ringold A unit is confined by the overlying Lower Mud unit. Upper, vadose zone units are the silty, calcium carbonate-rich Cold Creek Unit, sand-dominated facies of the Hanford formation, and gravel-dominated facies of the Hanford formation. The latter two units are moderate- to high-energy ice age flood deposits, respectively, and are in places overlain by more recent Holocene sands [9, 10].

Above the water table, variations in these vadose zone units have influenced the downward migration of CCl_4, and have trapped CCl_4 in both its dense, non-aqueous phase and its aqueous phase. This trapped CCl_4 acts as a source for further contamination [5]. Within the saturated zone, a small volume of aqueous CCl_4 has been transformed to chloroform ($CHCl_3$), creating a relatively low-concentration plume of $CHCl_3$ associated with CCl_4 groundwater contamination. Modeling $CHCl_3$ can therefore provide additional information regarding behavior of the CCl_4 plume.

In the 200 West Area, groundwater travels in a general eastward direction, flowing more toward the east-northeast in the northern portion of the Area, and more toward the east-southeast in the southern portion. Groundwater levels range between an elevation of about 139 m above sea level (asl) in the west, to 133 m asl in the east, and are slowly decreasing [6]. Flow rates vary, but tend to be less than 0.1 m/day [5]. Recent remediation has involved installation of pump and treat wells, with extraction wells in the heavily-contaminated central 200 West and injection wells about 1 km to the west. This treatment has altered groundwater levels and thus groundwater flow in the central 200 West Area.

Because of spatial variations in subsurface geology and spatiotemporal variations in groundwater flow, high-resolution spatial hydrogeological modeling is necessary to depict current (and predict future) contaminant migration. Sources providing information for such models include drillers' records, geologists' records, geophysical logs of boreholes, as well as groundwater monitoring data that provide contaminant concentrations and water levels. This study attempts to create a geological model along the primary flowpath of CCl_4 in the northern half of the 200 West Area, displaying the present-day extent of the plume and its interaction with subsurface geology.

Materials and Methods

A northeast-trending transect through the 200 West Area incorporating nineteen wells was identified. This transect begins near the source of carbon tetrachloride contamination and follows the curve of the plume's primary flow path (Fig. 1).

Drillers', geologists', and geophysical logs from wells along this transect were used, requiring systematization of the data recorded in these logs. Systematization follows PNL Procedures DO-6, DO-7, and DO-8, respectively, as detailed in Last et al., 2007 [10, 12]. For drillers' and geologists' logs, this procedure involves gleaning out information related to sediment class and composition, particle size, calcium carbonate content, color, moisture, roundness, and any relevant drilling procedures or other geologic characteristics associated with a certain depth. Sediment class and size were based on the Folk/Wentworth schemes. A total of 14 geologists' and drillers' logs (comprising 13 wells) were systematized and entered into the Hanford Borehole Geologic Information System (HBGIS), adding to the 6 transect wells already in the system. From HBGIS, sedimentary data were exported into LogPlot, graphing software that stratigraphically displays geologic information. Figure 4 displays a stratigraphic column created using LogPlot.

Geophysical data, primarily natural gamma (12 wells) along with spectral gamma (5 wells), were also entered into HBGIS. Data originated from three sources: recent digital records from the Hanford Site Groundwater Remediation Project, older digital records from the Pacific Northwest National Laboratory (PNNL) Log Database, and hard copy originals of graphical logs. Hard copy graphical logs were manually digitized using Engauge Software. Using a paired t-test, results from manual digitization were compared to digital records from wells 299-W6-10 and 299-W11-30 to determine accuracy of the manual process. Digital geophysical data from the three sources were entered into HBGIS, then graphed using LogPlot and compared to lithologic descriptions of the same wells. Using these data, a cross section along the primary groundwater flow path was modeled.

Special depth discrete and routine measurements of CCl_4 and $CHCl_3$ concentrations for all available wells were taken from the Hanford Virtual Library and the Hanford Environmental Information System (HEIS). Both types of data are presented in

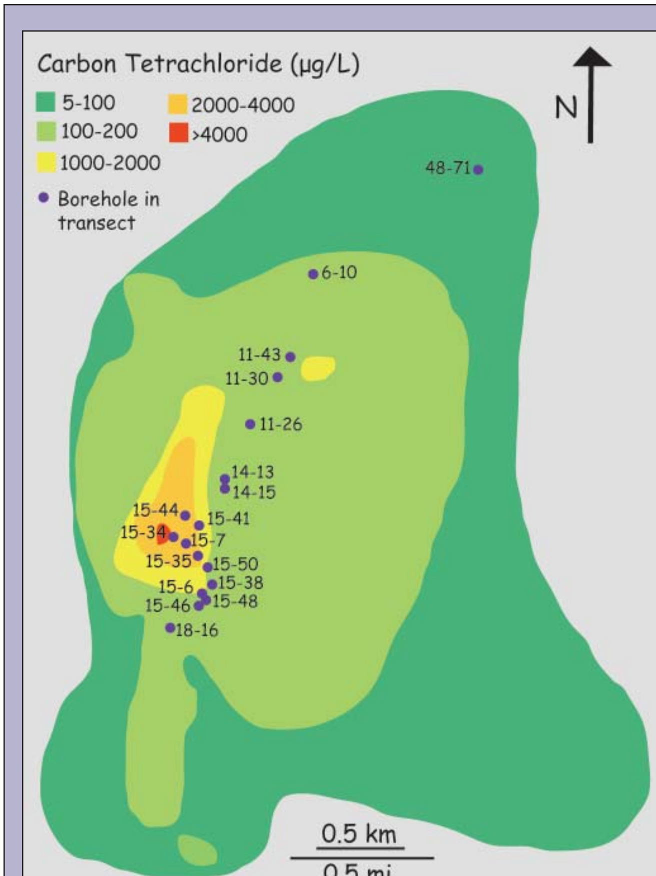

Figure 1. Carbon tetrachloride contaminant plume in 200 West Area aquifer, with boreholes included in this study's transect. All wells are located in the 200 West Area and are prefixed with 299-W, except for the most northern borehole (48-71), which is located just outside this Area and is prefixed 699-. Modified from Hartman et al., 2006 [6].

a

Well	Date	Depth (ft bgs)	$[CCl_4]$ (µg/L)	$[CHCl_3]$ (µg/L)
299-W18-16	11/22/2004	250.0	670	81
	12/9/2004	326.0	850	44
	12/15/2004	339.9	1.5	120
299-15-46	1/31/2006	226.5	1342	18
	2/1/2006	275.5	4096	37
299-W15-6	10/28/2004	318.2	110	1100
	11/14/2005	368.1	834	146
	11/14/2005	406.1	1003	235
299-W15-50	2/2/2005	285.0	1540	115
	2/7/2005	318.0	2000	52
299-W15-35	2/22/2006	254.0	2200	13
299-W15-7	8/14/1996	211.6	720	29
	8/14/1996	309.3	730	99
	2/22/2007	SI	2100	13
299-W15-34	2/22/2006	258.5	3200	18
	12/21/2005	280.6	3358	12
299-W15-41	2/15/2007	SI	1300	11
299-W15-44	2/15/2007	SI	2100	13
299-W14-15	-	-	-	-
299-W14-13	8/2/2006	SI	110	1.6
299-W14-1	-	-	-	-
299-W11-26	-	-	-	-
299-W11-43	6/1/2005	298.0	900	13
	6/9/2005	363.8	450	54
	6/21/2005	449.1	1100	46
299-W6-10	9/1/2005	SI	200	4.5
699-48-71	1/12/2007	SI	20	2.7

b

Well	Date	Depth (ft bgs)	$[CCl_4]$ (µg/L)	$[CHCl_3]$ (µg/L)
299-W15-46	1/31/2006	226.5	1342	18
	9/14/2004	229.2	330	150
	10/13/2005	232.5	1248	18
	10/13/2005	242.5	2116	22
	10/14/2005	253.5	2362	23
	10/11/2004	257.0	120	220
	2/1/2006	275.5	4096	37
	2/1/2006	286.5	2567	25
	10/19/2004	292.0	2918	413
	10/25/2004	297.5	286	1039
	10/28/2004	318.2	110	1100
	11/2/2004	338.9	32	690
	11/8/2004	357.0	258	353
	11/10/2004	365.6	1300	180
	11/15/2004	378.2	470	280
	11/23/2004	399.9	8.7	290
	11/30/2004	419.0	206	482
	1/13/2005	482.0	2.2	36
	1/26/2005	522.5	3	217

Table 1. a) Representative CCl_4 and $CHCl_3$ concentrations for all wells with available data in the transect. Concentrations are from depth discrete intervals except where marked SI, which are average concentrations over the screened interval of the well, and b) more detailed resolution of CCl_4 and $CHCl_3$ concentrations from well 299-W15-46. Peaks in CCl_4 and associated peaks in $CHCl_3$ are highlighted in blue.

Table 1a. Where more than one routine measurement was available, data from the closest date to February, 2007 was used. Although depth discrete contaminant concentrations for some wells are available at higher spatial resolutions, only select depths are displayed in Table 1a. Table 1b shows CCl_4 and $CHCl_3$ concentrations in well 299-W15-46 in more detail. Using these data, extent and concentrations of the CCl_4 and $CHCl_3$ plumes were estimated. Only aqueous CCl_4 within the unconfined aquifer was identified, and both plumes were interpreted to have failed to permeate the Lower Mud unit where the unit is continuous.

Results

Data from manual digitization of geophysical logs is consistent with data regarding stratigraphic depths of peaks evident in digital geophysical records. However, actual counts per second values vary, sometimes considerably, between the two record types (Fig. 2). Discrepancies between the records appear clustered by depth, suggesting a systematic error in digitization.

Subsurface geology is modeled in a curvilinear transect through the central to northeastern 200 West Area, as displayed in Figure 3. Units generally dip toward the southwest, but vary in thickness and continuity; a short summary of lithofacies trends are presented. The Ringold Lower Mud unit thins toward the northeast, eventually pinching out shortly beyond well 299-W11-43. However, the underlying Ringold A unit thickens toward the northeast, contacting the Ringold E unit where the Lower Mud is absent and thus connecting the confined and unconfined aquifers. The water table in this portion of the 200 West Area generally decreases in elevation along the transect toward the northeast.

Above the water table and the Ringold E unit, the Cold Creek Unit extends throughout the transect, ranging in thickness from approximately 4 to 16 m. A thin, discontinuous caliche layer is found at the bottom of this unit. A lower sand-dominated and an upper gravel-dominated subunit of the Hanford formation are present throughout the transect, with the transition from the lower to upper subunits nearly always a sharp contact. Holocene sand,

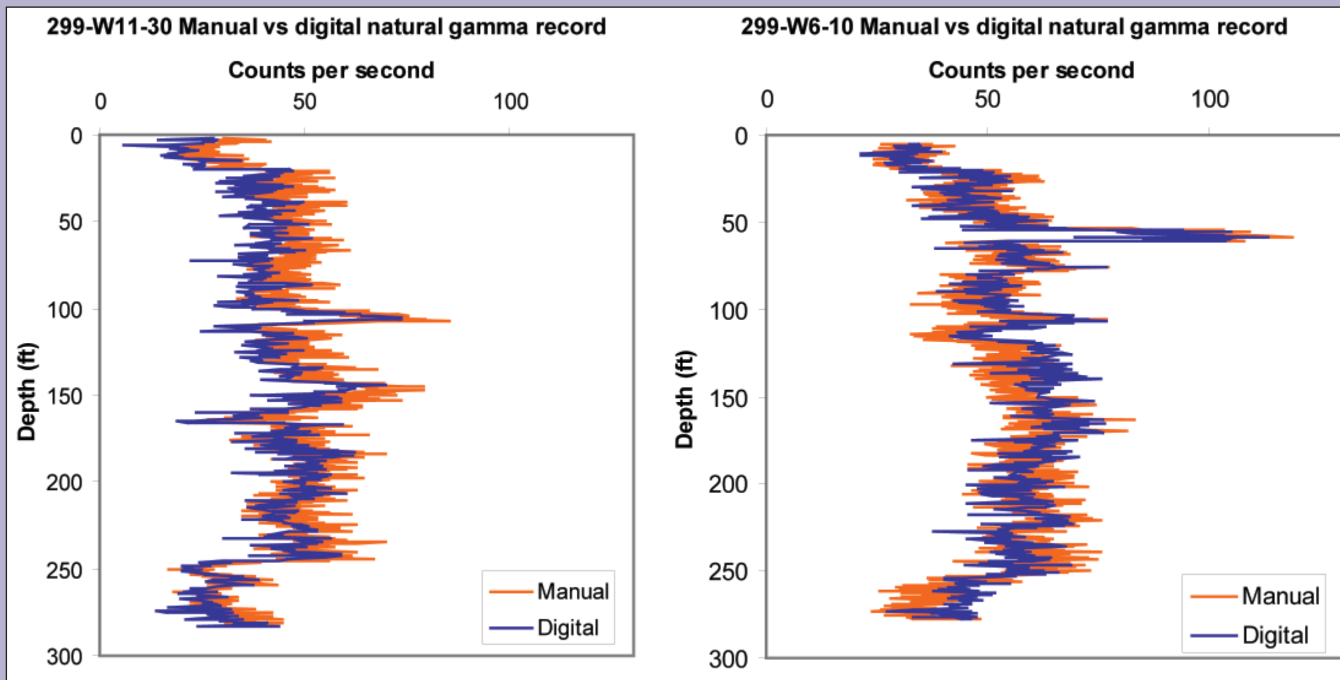

Figure 2. Comparison of manually digitized and digital record of natural gamma counts per second from wells 299-W6-10 and 299-W11-30.

as it is elsewhere in the 200 West Area, is discontinuous along the transect.

Results show an extensive low-concentration area (greater than 5 µg/L) of the CCl_4 plume, with increasing concentrations (greater than 1000 µg/L) extending over 1200 m along the transect (Fig. 3). While the CCl_4 plume sits above the Lower Mud sequence where the unit is present, discontinuities in the unit to either side of the transect have permitted CCl_4 to permeate into the confined (Ringold A) aquifer in the northeast of the 200 West Area. Highest CCl_4 concentrations are located around well 299-W15-46 and wells 299-W15-34 through 299-W15-44; both 299-W15-34 and 299-W15-44 are groundwater extraction wells for the pump and treat remediation system. Finer-grained sand or mud layers frequently form the bottom boundary of these high concentration areas (Fig. 3).

Chloroform concentrations are usually one to two orders of magnitude less than those of CCl_4, with the exception of $CHCl_3$ concentrations of up to 1,100 µg/L around well 299-W15-46 in central 200 West. When considering sample records from discrete depths within individual wells, higher concentrations of $CHCl_3$ are generally located near higher concentrations of CCl_4. Furthermore, in many instances peaks in $CHCl_3$ concentrations occur stratigraphically lower (by less than 8 m) than the associated peak in CCl_4 concentration (Table 1b, Fig. 3). This trend is well represented by depth discrete CCl_4 and $CHCl_3$ concentrations from well 200-W15-46 (Table 1b).

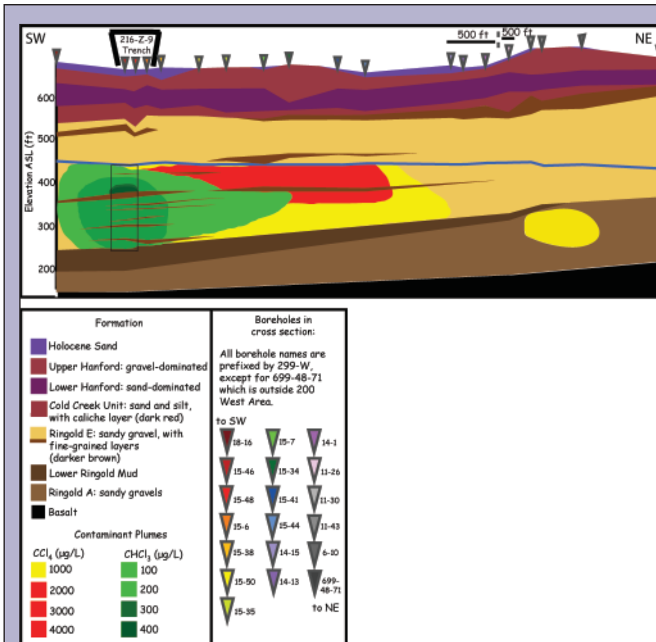

Figure 3. Cross section along primary groundwater flow path showing general stratigraphy, borehole locations, and carbon tetrachloride and chloroform concentrations. Note water table (dark blue line) above contaminated groundwater. Trench 216-Z-9 is located near wells 299-W15-46, 299-W15-48, and 299-W15-6. A close-up of the inset box is displayed in Figure 4.

Discussion and Conclusion

Concentrations of carbon tetrachloride in the groundwater of the 200 West Area appear to be affected by a combination of sediment type and unit continuity, down-gradient groundwater flow, injection and extraction wells, and to a lesser extent reductive dechlorination of CCl_4 to $CHCl_3$. At present, the two areas of highest CCl_4 concentration along this study's northeast-southwest transect are located below the 216-Z-9 trench (Fig. 3) and at extraction wells. Those locations are precisely where highest concentrations would be expected during a successful remediation

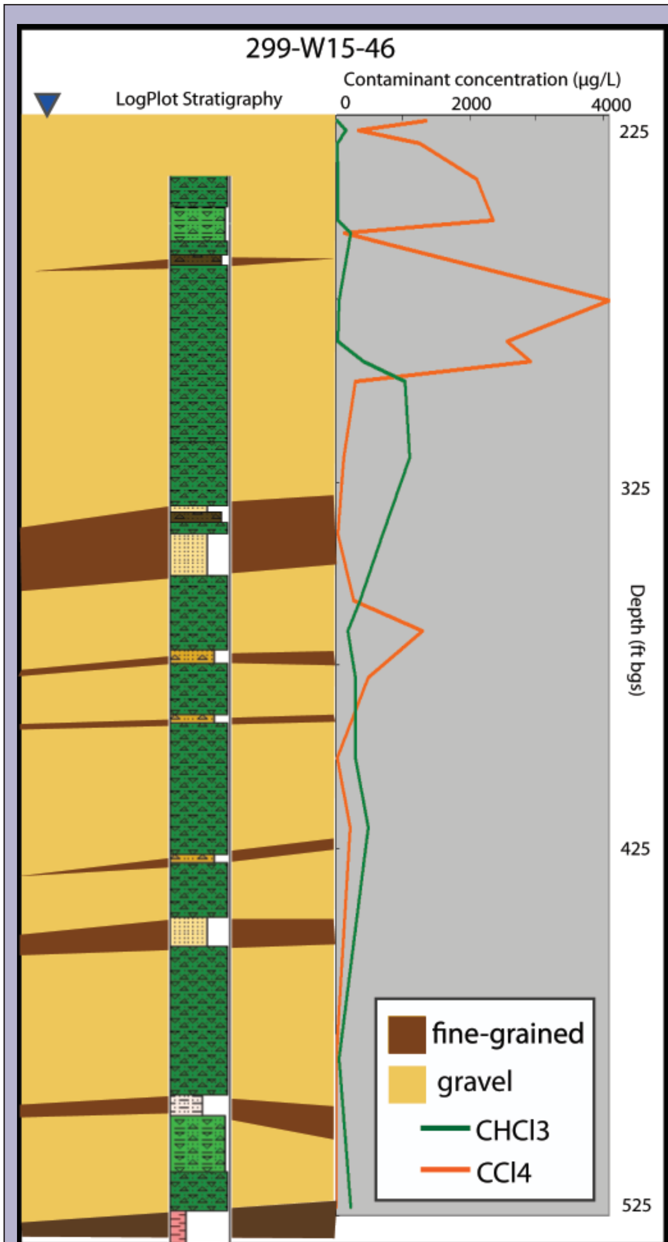

Figure 4. Comparison of stratigraphy to CCl_4 and $CHCl_3$ concentrations of the unconfined aquifer at borehole 299-W15-46. Stratigraphy is modeled from LogPlot data, and contaminant concentrations are extracted from HEIS. Gravel-dominated sediments are shown in green on the stratigraphic LogPlot column, and sand-dominated sediments are shown in brown, both of which are part of the Ringold E formation. Water level is at the top of the column, and the Ringold Lower Mud bounds the bottom of the column.

process, and this pattern was found in other, larger-scale studies of CCl_4 in the 200 West Area [6]. This demonstrates some success in the pump and treat remediation effort.

During discussion of contaminant concentrations presented in this report, it should be remembered that data was collected over a 2.5 year time span. Thus, some changes in concentrations by depth are partially an artifact of the sampling time.

Stratigraphic control on downward migration of CCl_4 is evident at several layers of fine-grained sediment (Figs. 3, 4). The depth discrete record of well 299-W15-46, which exhibits the highest CCl_4 concentration along this transect, shows that all concentrations above 2000 µg/L are confined between two thin layers of sand (Figs. 3, 4). Highest recorded CCl_4 concentrations for wells 299-W18-16, 299-W15-6, and 299-W15-50 are all located at thin (less than 2 m) layers of relatively fine-grained material. With the exception of 299-W15-7, all other wells in this transect with a depth discrete record of CCl_4 concentration were sampled over a saturated interval that only included gravels. This indicates that thin, fine-grained layers within the generally coarse-grained Ringold E unit partially inhibit downward CCl_4 migration.

Frequent presence of $CHCl_3$ peaks stratigraphically below those of CCl_4 suggest that if $CHCl_3$ is present primarily because of CCl_4 dechlorination, variations in sediment grain size have a strong effect on this reaction. Alternative sources of $CHCl_3$ include past waste discharges into a nearby tile field [6] and impurities in the originally disposed CCl_4. If $CHCl_3$ and CCl_4 have different source locations, comparison between the stratigraphic controls on the two contaminants is less accurate. Additionally, sampling resolution is generally coarse, with records 5–10 m apart, resulting in uncertainty in actual peak values and locations. Therefore, peaks in concentrations for both contaminants may be stratigraphically closer than they appear at this sampling resolution.

Despite these uncertainties, data from several wells in this transect (e.g. 299-W15-46, 299-W15-50, and 299-W18-16) indicate that peaks in $CHCl_3$ are associated with the transformation of CCl_4 (Table 1b). Carbon tetrachloride is rapidly dechlorinated into $CHCl_3$ when reacted with Fe^{2+}:

$$CCl_4 + 2Fe^{2+}(Porph) + H^+ \rightarrow CHCl_3 + Fe^{3+}(Porph) + Cl^- \quad (1)$$

where Fe^{2+}(Porph) is a reduced iron porphyrin hydroxide found under iron-reducing conditions [13, 14]. In borehole samples, these reducing conditions are indicated by green, gray, blue, or olive brown sediments. Sediments in the 200 West Area possessing iron necessary for the above reaction to occur include carbonates and those incorporating iron-rich basalt.

For individual wells with sufficient data, the presence of reducing conditions and iron-containing minerals can tentatively be related to CCl_4 and $CHCl_3$ concentrations at a given depth. The borehole record for well 299-W18-16 identifies olive brown sediment at the only recorded depth at which $CHCl_3$ concentrations are greater than those of CCl_4. The record for well 299-W15-46 shows that the highest ratio of $CHCl_3$ to CCl_4 above the Lower Mud Unit is found in greenish to gray sediment. While these few examples cannot conclusively indicate a correlation between reduced, iron-containing sediments and high transformation rates of CCl_4 to $CHCl_3$, they do suggest that further study of this relationship is warranted.

Most studies documenting the stratigraphy of the Hanford Site describe sedimentary units that are generally between 10 and 100 m thick [1, 10]. While the scale of these divisions is useful in predicting low-resolution contaminant migration, heterogeneities in mineral composition, grain size, and a layer's capability to provide a reducing environment vary on the scale of decimeters to meters (Fig. 3). These heterogeneities appear to strongly influence transport of $CHCl_3$ and CCl_4, and dechlorination of CCl_4. To accurately predict future contaminant migration, small-scale subunits of the accepted sedimentary units should be identified and mapped throughout the CCl_4 plume area. The stratigraphic model presented in this study provides a guide for beginning this work, but is limited in its coverage. During mapping, particular attention should be paid to sediment color and composition (indicators of reducing conditions), and to grain size. In addition, prediction of contaminant transport would be benefited by geochemical studies comparing sediment color to reducing conditions on the Hanford Site.

Acknowledgements

The project was completed at the Pacific Northwest National Laboratory, and funded by the Remediation Decision Support Project managed by Tom Fogwell (Fluor Hanford) and the U.S. Department of Energy's Office of Science SULI Program. I am incredibly grateful to my mentor, George Last, who answered each of my questions with a drawing, a book, and a joke. Thanks also to Rob Mackley and Dave Lanigan, who repeatedly helped me to dig out hard-to-find information, and to Karen Wieda who energetically made me feel welcome at the lab.

References

[1] G.W. Gee, M. Oostrom, M.D., Freshley, M.L. Rockhold, and J.M., Zachara, "Hanford Site vadose zone studies: an overview," Vadose Zone Journal, v. 6, no. 4, p. 899-905, 2007.

[2] H.G. Wilshire and I. Friedman, "Contaminant migration at two low-level radioactive waste sites in arid western United State- a review", Environmental Geology, v. 37, no. 1-2, p. 112-123, 1999.

[3] M.J. Truex, C.J. Murray, C.R. Cole, R.J. Cameron, M.D. Johnson, R.S. Skeen, and C.D. Johnson, "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, 2001.

[4] C.J. Murray, Yi-Ju Bott, and M.J. Truex, "Persistence and Inventory of Carbon Tetrachloride in the 200 West Area of the Hanford Site," Pacific Northwest National Laboratory, Richland, Washington, 2007.

[5] W.L. Bratton, K.R. Moser, and J.D. Doughty, "Carbon Tetrachloride Dense Non-Aqueous Phase Liquid (DNAPL) Source Term Interim Characterization Report," DOE/RL 2006-58, U.S. Department of Energy, Richland, Washington, 2006.

[6] M.J. Hartman, L.F. Morasch, W.D. Webber, "Hanford Site Groundwater Monitoring for Fiscal Year 2005," PNNL 15670, Pacific Northwest National Laboratory, Richland, Washington, 2006.

[7] J.P. McKinley, J.M. Zachara, J. Wan, D.E. McCready, and S.M. Heald, "Geochemical controls on contaminant uranium in vadose Hanford Formation sediments at the 200 Area and 300 Area, Hanford Site, Washington," Vadose Zone Journal, v. 6, no. 4, p. 1004-1017, 2007.

[8] D.G. Horton, G.V. Last, T.J. Gilmore, B.N. Bjornstad, and R.D. Mackley, "A catalogue of geologic data for the Hanford Site," PNNL-13653, Pacific Northwest National Laboratory, Richland, WA, 2005.

[9] S.P. Reidel, and M.A. Chamness, "Geology Data Package for the Single-Shell Tank Waste Management Areas at the Hanford Site," Pacific Northwest National Laboratory, Richland, Washington, PNNL-15955, 2007.

[10] J.M. Zachara, J. Serne, M. D. Freshley, F. Mann, F. Anderson, M. Wood, T. Jones, and D. Myers, "Geochemical processes controlling migration of tank wastes in Hanford's vadose zone," Vadose Zone Journal, v. 6, no. 4, p. 985-1003, 2007.

[11] G.V. Last, C.J. Murray, D.A. Bush, E.C. Sullivan, M.L. Rockhold, R.D. Mackley, and B.N. Bjornstad, "Standardization of borehole data to support vadose zone flow and transport modeling," Vadose Zone Journal, v. 6, no 4., p. 906-912, 2007.

[12] PNL-MA-567, Procedures for Groundwater Investigations. DO-6, DO-7, DO-8, Pacific Northwest National Laboratory, Richland, Washington, 2006.

[13] Schwartzenbach, et al., Environmental Organic Chemistry. New York: Wiley-Interscience, 1993.

[14] R. Allen-King, "Geochemical and Physical Aquifer Property Heterogeneity: a Multi-scale Sedimentologic Approach to Reactive Solute Transport," State University of New York at Buffalo, 2006.