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U.S. DEPARTMENT OF
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Project Work Plan Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

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MJ Truex
JS Fruchter

June 2006

Pacific Northwest
NATIONAL LABORATORY

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Pacific Northwest National Laboratory
Operated by Battelle for the U.S. Department of Energy
Richland, Washington 99352

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1.0 Introduction

Between 1955 and 1973, an estimated 750,000 kg of carbon tetrachloride were discharged to the soil in the 200 West Area of the Hanford Site as part of the plutonium production process. Of this amount, some carbon tetrachloride reached the groundwater more than 70 m below the ground surface and formed a plume of 10 km^2. Recent information has shown that the carbon tetrachloride plume extends to a depth of at least 60 m below the water table. Some carbon tetrachloride has been degraded either by the original process or subsequent transformations in the subsurface to form a co-existing chloroform plume.

Although current characterization efforts are improving the conceptual model of the source area, more information is needed to effectively assess the fate and transport of carbon tetrachloride and chloroform to support upcoming remediation decisions for the plume. As noted in a simulation study by Truex et al. (2001), parameters describing porosity, sorption, and abiotic degradation have the largest influence on predicted plume behavior. The work proposed herein will improve the ability to predict future plume movement by better quantifying abiotic degradation mechanisms and rates. This effort will help define how much active remediation may be needed and estimate where the plume will eventually stabilize – key factors in determining the most appropriate remedy for the plume.

A preliminary evaluation of remediation alternatives for the plume (Siegel et al. 2003) drew the following conclusions:

> *"The conditions present at the 200 West Area appear favorable to the successful implementation of the MNA [Monitored Natural Attenuation] approach. Application of this technique in conjunction with source-term removal or containment and control in both the vadose zone and the ground water could be a potentially cost-effective strategy. The most significant requirement is to identify and quantify the natural attenuation mechanisms in both the soil and ground water at Hanford."*

Of the possible natural attenuation mechanisms, biodegradation is not likely to contribute significantly (Truex et al. 2001). In contrast, abiotic degradation processes such as hydrolysis and reduction are likely to contribute significantly (Truex et al. 2001) and, therefore, are important to understand in the context of selecting how active remedies will be applied to the carbon tetrachloride/chloroform plume at Hanford. Previous field and modeling efforts have focused on determining the impacts of other attenuation mechanisms including dispersion and dilution processes and carbon tetrachloride sorption to Hanford sediments (Riley et al. 2005). The abiotic degradation processes, however, are not well understood.

Previous determinations of the hydrolysis rate for carbon tetrachloride in water (i.e., homogeneous hydrolysis) have been made, but they involved experiments at high temperature (>70°C). Arrhenius parameters developed from these data were used to extrapolate the hydrolysis rate to ambient groundwater temperatures. However, the uncertainty in these values is so large that the current information is not sufficient to distinguish whether the attenuation rate by hydrolysis will have a significant impact on the plume. To decrease this uncertainty, in fiscal year (FY) 2006 the Hanford Groundwater Project initiated a study to determine the homogeneous hydrolysis rate of carbon tetrachloride at temperatures closer to ambient groundwater temperatures. The homogeneous hydrolysis study will also provide initial observations of possible sediment effects on the carbon tetrachloride degradation rate. These heterogeneous effects may involve both hydrolysis and electron-transfer pathways, although the generally oxidizing nature of the Hanford subsurface suggests that electron-transfer may not contribute significantly.

Two relevant topics not being addressed by the carbon tetrachloride homogeneous hydrolysis study may be important to quantify the overall attenuation capacity for the carbon tetrachloride and chloroform plume. First, the study is not investigating the hydrolysis rate for chloroform, a prominent co-contaminant with carbon tetrachloride. Under homogeneous conditions, chloroform degrades by both neutral and base-catalyzed hydrolysis. As with carbon tetrachloride, extrapolation of high-temperature data has been made and suggests a half-life under Hanford groundwater conditions that is several times slower than that for carbon tetrachloride but with comparable uncertainty. Again, as with carbon tetrachloride, the overall abiotic degradation rate of chloroform at ambient temperatures may be a combination of homogeneous and heterogeneous hydrolysis reactions as well as other redox-related heterogeneous reactions. Second, the carbon tetrachloride homogeneous hydrolysis study does not include an experimental approach that would allow anything to be said about the mechanism of a possible heterogeneous effect. In particular, experiments with a variety of mineral surfaces such as clays, zeolites, feldspars, and iron oxides are needed if a robust predictive capability is to be developed for heterogeneous effects on carbon tetrachloride or chloroform hydrolysis in the Hanford subsurface. Unfortunately, the already sparse literature on the hydrolysis of carbon tetrachloride and chloroform is completely silent on the question of heterogeneous effects for these two compounds.

2.0 Technology Description

The work described in this plan is designed to complement and leverage the work recently initiated in the carbon tetrachloride homogeneous hydrolysis project. We will address the uncertainty in the homogeneous hydrolysis rate for chloroform using an approach similar to that in the carbon tetrachloride homogeneous hydrolysis project. We will also conduct thorough investigations of the possible impact of mineral surfaces on the hydrolysis rates of both carbon tetrachloride and chloroform. Although the final results of this work will require several years because of the slow hydrolysis rates expected at near-ambient temperatures, the major cost associated with the work is in the experimental set up during the first year. We anticipate that funding beyond the mandate of the current opportunity will be made available to continue sampling and analysis in the out years. Even if such funding is not available, the additional information gathered in a roughly 2-year time span will be of great value in selecting the appropriate application of active remediation in conjunction with natural plume attenuation. Ultimately, the results of this proposed work will help provide a scientific basis for predicting the contribution of abiotic degradation processes to remediation of carbon tetrachloride and chloroform at the Hanford Site.

3.0 Project Scope

The objectives of the work are to determine (1) the neutral and base-catalyzed homogeneous hydrolysis rates for chloroform under near-ambient temperatures, (2) the impact and mechanisms of representative Hanford mineral surfaces on the hydrolysis of carbon tetrachloride at near-ambient temperatures, and (3) the impact and mechanisms of representative Hanford mineral surfaces on the neutral and base-catalyzed hydrolysis of chloroform at near-ambient temperatures.

The work will be organized into five major tasks: Task 1 will provide project management support, Task 2 will focus on the neutral and base-catalyzed homogeneous rates of chloroform, Task 3 will focus on the heterogeneous rate of carbon tetrachloride, Task 4 will focus on the neutral and base-catalyzed heterogeneous rates of chloroform, and Task 5 will prepare annual letter reports and a final published Pacific Northwest National Laboratory (PNNL) report. Our approach is designed to succeed in the shortest time possible while producing robust data that will withstand the critical scrutiny of scientists, decision-makers, and stakeholders. Detailed descriptions of each task is included in the following sections.

3.1 Task 1: Project Management

Plan, organize, and provide top-level guidance and direction for overall project performance. Also provide project-level cost and schedule control, tracking, and reporting. Coordinate the Columbia River Protection Supplemental Technologies Project work scope with the U.S. Department of Energy (DOE), Richland Operations, the Groundwater Remediation and Closure Assessment Project, and the DOE Office of River Protection, including participation in planning, peer reviews, and periodic project meetings.

3.2 Task 2: Neutral and Base-Catalyzed Homogeneous Hydrolysis of Chloroform

Subtask 2.1 – Develop Detailed Experimental Plan and Methods. Develop detailed experimental plan and methods to determine the neutral and base-catalyzed hydrolysis of chloroform. At present, the overall experimental design involves collection of data at six temperatures covering the range of 20°–70°C. Samples will be incubated in sterile deionized water adjusted to one of three initial pHs with H_2SO_4 or NaOH (3.0, 7.5, or 12.7), at one of two concentrations (40 or 400 ppm), for periods of up to 5 years. We will conduct five replicate analyses for each treatment combination at each of ten times during the experiment. Thus, the total number of experimental units is 6x3x2x5x10 = 1800.

Subtask 2.2 – Conduct Test. Prepare samples, incubate at specified temperatures for appropriate time periods, terminate samples, and analyze fluids/headspace to determine extent of chloroform degradation by hydrolysis.

We plan to conduct parallel experiments in two geometries and at two locations. At PNNL, we plan on preparing samples using 1.0 mL glass ampules with about 30% headspace sealed by an automatic ampule sealer. A separate set of experiments will be conducted at SUNY-Cortland using minimal headspace Pyrex glass bulbs (Jeffers et al. 1989, 1994) drawn from 7-mm Pyrex tubing and containing about 350 µL of aqueous solution and 15 µL of headspace. These bulbs allow simultaneous filling of multiple specimens with identical solution. At both locations, samples will consist of two starting concentrations (40 and 400 ppm) of chloroform prepared under conditions to ensure no microbial activity. Perchloroethene (PCE), which has a hydrolysis half-life of 10^9 years (Jeffers et al. 1989), will serve as an internal standard. All tubes and solutions will be precleaned and either heat or filter sterilized. To establish an accurate estimate of temperature dependence, samples will be incubated at 20°C, 30°C, 40°C, 50°C, 60°C, and 70°C using air-flow incubators with a nominal accuracy of 0.1°C. The higher temperatures provide a linkage with existing high temperature data to check experimental accuracy. Samples will be taken and analyzed periodically for a total of ten sampling periods, with specific sampling times depending on the expected hydrolysis rate at a given temperature. As many as five replicates will be analyzed at each time period, depending on the precision obtained. Sampling will involve breaking the tip of the ampule, immediately extracting a sample by gas-tight syringe for direct injection into a sealed gas chromatography (GC) vial containing hexane, extracting a second sample for analysis of chloride concentration by ion chromatography, and then transferring the remainder of the solution to a small cylindrical vial for determination of pH by microelectrode calibrated to National Institute for Standards and Technology traceable standards. The sample in the GC vial will then be analyzed for chloroform, PCE, and possible organic degradation products using GC with mass spectrometry or electron-capture detection.

For each temperature, second-order rate data will be calculated after four samplings. When second-order rate constants for at least four temperatures are available, an Arrhenius plot will be made, and hydrolysis half-lives with 95% confidence intervals determined for temperatures down to 15°C. These calculations will be updated with data from each successive sampling period. The expectation is that the confidence intervals will be tightest for the highest temperatures and highest pHs, and that the temperature at which an acceptable confidence interval is obtained will decrease with each successive sampling. Sampling will continue until either all samples have been analyzed or an acceptable confidence interval is obtained for 15°C, whichever occurs first.

3.3 Task 3: Heterogeneous Hydrolysis of Carbon Tetrachloride

Subtask 3.1 – Develop Detailed Experimental Plan and Methods. Develop detailed experimental plan and methods to determine the rate of hydrolysis of carbon tetrachloride in contact with solid phases representative of those found in the subsurface at Hanford 200 West Area, 200-ZP-1 Operable Unit. This subtask will be performed at the same time as Subtask 4.1 as they are very similar in nature.

We expect that the experimental approach for determination of heterogeneous hydrolysis of carbon tetrachloride will differ in some respects from that of Task 2 because of logistical constraints. Data will be collected at four temperatures (20°C, 30°C, 40°C, and 50°C) and at one concentration (40 ppm). Samples will be incubated in one of six environments consisting of sterile Hanford groundwater alone or in the presence of fine-grained (<53 μm) sediment or mineral powder. The sediment will consist of uncontaminated silt and clay from the lower Ringold Formation near the 200 West Area of the Hanford Site. Four representative minerals ground to fine-silt size using corundum grinding elements in a McCrone micronizing mill will also be suspended in the sterile Hanford groundwater. As in Task 2, we will conduct five replicate analyses for each treatment combination at each of ten times during the experiment. Thus, the total number of experimental units is 4x1x6x5x10 = 1200.

Subtask 3.2 – Obtain and Characterize Solids. Identify, obtain, and characterize the solids (sediment and mineral samples) used to determine heterogeneous rates of hydrolysis. This subtask will be performed at the same time as Subtask 4.2 as they will involve the same solids.

Subtask 3.3 – Conduct Test. Prepare samples, incubate at specified temperatures for appropriate time periods, terminate samples, and analyze fluids/headspace to determine extent of carbon tetrachloride degradation by hydrolysis in the presence of solid material representative of the Hanford 200 West Area, 200-ZP-1 Operable Unit subsurface.

As in Task 2, we plan to conduct parallel experiments in two geometries and at two locations. At PNNL, we plan on preparing samples using 1.0 mL glass ampules with about 30% headspace sealed by an automatic ampule sealer. A separate set of experiments will be conducted at SUNY-Cortland using minimal headspace Pyrex glass bulbs (Jeffers et al. 1989, 1994) drawn from 9-mm Pyrex tubing and containing about 1 mL of aqueous sample and 20 µL of headspace. Bulbs will be drawn at one end, filled to about 60% of capacity with a known mass of dry sediment/mineral powder, and then the second end will be drawn before filling as in Task 2. The Hanford groundwater will be filter sterilized. The sediment and mineral powders will be heat sterilized. Sampling and analysis will be performed in the same manner as described in Task 2 with the exception that no pH values will be measured (the carbon tetrachloride hydrolysis reaction is not sensitive to pH).

3.4 Task 4: Neutral and Base-Catalyzed Heterogeneous Hydrolysis of Chloroform

Subtask 4.1 – Develop Detailed Experimental Plan and Methods. Develop detailed experimental plan and methods to determine the rate of hydrolysis of chloroform in contact with solid phases and pH conditions that are representative of those found in the subsurface at Hanford 200 West Area, 200-ZP-1 Operable Unit. This subtask will be performed at the same time as Subtask 3.1 as they are very similar in nature.

Subtask 4.2 – Obtain and Characterize Solids. Identify, obtain, and characterize the solids (sediment and mineral samples) used to determine heterogeneous rates of hydrolysis. This subtask will be performed at the same time as Subtask 3.2 as they will involve the same solids.

Subtask 4.3 – Conduct Test. The experimental approach for heterogeneous hydrolysis of chloroform will closely follow that of Task 3 with the exception that pH will be determined as in Task 2 to allow calculation of the second-order rate constant. We expect some variability in pH stemming from reactions of the groundwater with the different sediment/mineral solids, but, to avoid artifacts, we will not attempt to adjust pH to a common starting value. The total number of experimental units is 4x1x6x5x10 = 1200.

3.5 Task 5: Reporting

Subtask 5.1 – Prepare Annual FY Letter Reports. A letter report will be prepared at the end of FY 2006 and FY 2007 that summarizes the work accomplished and data obtained during the fiscal year.

Subtask 5.2 – Prepare and Publish Final Report. At the end of the funding cycle (FY 2008), a formal project report will be prepared and published as a PNNL report that summarizes the results over the entire project.

4.0 Assumptions

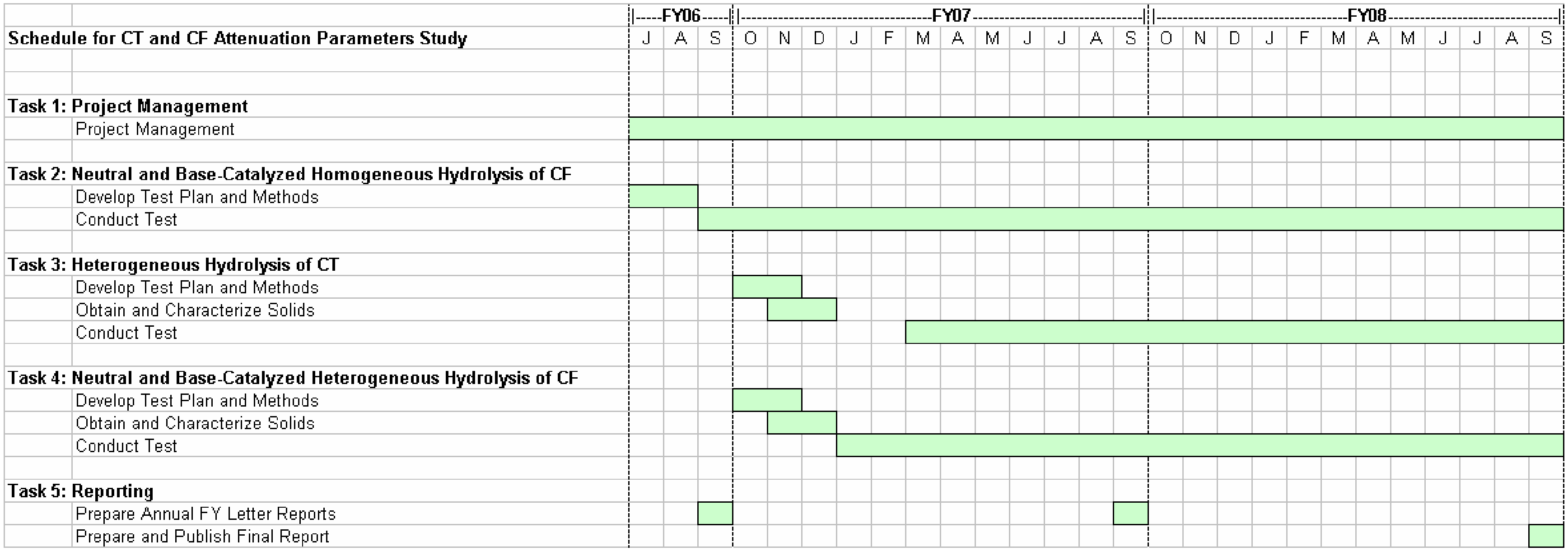
The following assumptions pertain to this scope of work:

- The project will start on or before July 1, 2006.
- A project-specific quality assurance plan (QAP) is required. This will describe the type of experiments, chemical, and the associated detection limits, duplicates, blind duplicates, and other quality assurance information.
- The schedule shown in this proposal will be approved by DOE and the appropriate regulatory agencies.

5.0 Schedule

A detailed schedule for the carbon tetrachloride and chloroform attenuation parameter study is shown in Table 1.

Table 1. Schedule for the Carbon Tetrachloride and Chloroform Attenuation Parameters Study



		FY06			FY07												FY08											
Schedule for CT and CF Attenuation Parameters Study		J	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F	M	A	M	J	J	A	S
Task 1: Project Management																												
	Project Management	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 2: Neutral and Base-Catalyzed Homogeneous Hydrolysis of CF																												
	Develop Test Plan and Methods	🟩	🟩																									
	Conduct Test			🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 3: Heterogeneous Hydrolysis of CT																												
	Develop Test Plan and Methods				🟩	🟩																						
	Obtain and Characterize Solids					🟩	🟩																					
	Conduct Test									🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 4: Neutral and Base-Catalyzed Heterogeneous Hydrolysis of CF																												
	Develop Test Plan and Methods				🟩	🟩																						
	Obtain and Characterize Solids					🟩	🟩																					
	Conduct Test							🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩	🟩
Task 5: Reporting																												
	Prepare Annual FY Letter Reports			🟩												🟩												
	Prepare and Publish Final Report																											🟩

6.0 Budget

The total budget for this plan is estimated to be approximately $309,000. Tables 2 and 3 show the cost summary and task summary.

Table 2. Cost Summary

1. Direct Labor (Schedule B)	Total	FY06	FY07	FY08
Research Scientist/Eng	$73,282	$21,675	$37,025	$14,582
Science & Engineering Associates	$0	$0	$0	$0
Administrative Professionals	$0	$0	$0	$0
Technicians	$17,976	$2,884	$11,373	$3,719
Crafts	$0	$0	$0	$0
Clerical/Secretarial	$0	$0	$0	$0
Total Direct Labor	$91,258	$24,559	$48,398	$18,301
2. Overhead				
Organization OverHead (Schedule C)	$49,020	$12,212	$26,932	$9,877
Program Dev. and Mgmt	$28,625	$7,650	$15,415	$5,559
Lab Directed R&D	$14,820	$3,906	$7,981	$2,934
Total Overhead	$62,824	$15,956	$34,366	$12,502
3. Travel (Schedule F)				
Transportation	$0	$0	$0	$0
Subsistence	$0	$0	$0	$0
Total Travel	$0	$0	$0	$0
4. Other Direct Costs (Schedule D)				
Procurement Svc Charges	$448	$355	$61	$32
SubContract Admin.	$2,938	$1,020	$1,475	$443
Other Non-Labor Dir. Costs	$12,880	$3,007	$7,432	$2,441
Total Other Direct Costs	$16,266	$4,381	$8,969	$2,916
5. Value Added	$170,349	$44,897	$91,733	$33,719
6. Other Indirect Costs	$0	$0	$0	$0
7. Direct Materials (Schedule E)				
Miscellaneous Materials	$7,831	$3,518	$2,726	$1,587
SubContract/OHC	$65,699	$17,737	$36,883	$11,079
Total Direct Materials	$73,530	$21,255	$39,609	$12,666
8. LDRD	$14,820	$3,906	$7,981	$2,934
9. Gen. & Admin Exp.	$43,098	$11,359	$23,208	$8,531
10. SubTotal	$301,797	$81,416	$162,530	$57,850
11. Service Assessment	$7,243	$1,954	$3,901	$1,388
12. Total PNNL Cost	$309,040	$83,370	$166,431	$59,238
13. Fed Admin Charge	$0	$0	$0	$0
14. Total COST + FED Admin	$309,040	$83,370	$166,431	$59,238

Table 3. Cost Summary by Subtask

		FY06		
1. Direct Materials Svc Chgs	Total	Project Management	Neutral & Base-Catalyzed	Data Analysis & Reporting
Procurement Svc Charges	$448	$0	$355	$0
SubContract Admin.	$2,938	$0	$1,020	$0
Total Dir. Mat. Svc Chgs	$3,386	$0	$1,375	$0
2. Direct Labor				
Research Scientist/Eng	$73,282	$1,998	$17,467	$2,210
Science & Engineering Associates	$0	$0	$0	$0
Administrative Professionals	$0	$0	$0	$0
Technicians	$17,976	$0	$2,884	$0
Crafts	$0	$0	$0	$0
Clerical/Secretarial	$0	$0	$0	$0
Total Direct Labor	$91,258	$1,998	$20,351	$2,210
3. Overhead				
Organization OverHead	$49,020	$600	$10,624	$988
Program Dev. and Mgmt	$13,804	$166	$3,372	$206
Total Overhead	$62,824	$767	$13,996	$1,194
4. Travel				
Transportation	$0	$0	$0	$0
Substistence	$0	$0	$0	$0
Total Travel	$0	$0	$0	$0
5. Other Direct Costs				
Non-Labor Dir. Costs	$12,880	$176	$2,590	$241
Total Other Direct Costs	$12,880	$176	$2,590	$241
6. Value Added	$170,349	$2,941	$38,312	$3,644
7. Other Indirect Costs	$0	$0	$0	$0
8. Direct Materials				
Miscellaneous Materials	$7,831	$0	$3,518	$0
SubContract/OHC	$65,699	$0	$17,737	$0
Total Direct Materials	$73,530	$0	$21,255	$0
9. LDRD	$14,820	$256	$3,333	$317
10. Gen. & Admin Exp.	$43,098	$744	$9,693	$922
11. SubTotal	$301,797	$3,941	$72,593	$4,883
12. Service Assessment	$7,243	$95	$1,742	$117
13. Total PNNL Cost	$309,040	$4,035	$74,335	$5,000
14. Fed Admin Charge	$0	$0	$0	$0
15. Total COST + FED Admin	$309,040	$4,035	$74,335	$5,000

Table 3. (contd)

	FY07				
1. Direct Materials Svc Chgs	Project Management	Neutral & Base-Catalyzed	Heterogeneous Hydrolysis	Performance Assessment Sampling	Data Analysis & Reporting
Procurement Svc Charges	$0	$11	$32	$19	$0
SubContract Admin.	$0	$237	$619	$619	$0
Total Dir. Mat. Svc Chgs	$0	$248	$651	$638	$0
2. Direct Labor					
Research Scientist/Eng	$3,959	$5,464	$12,696	$12,696	$2,210
Science & Engineering Associates	$0	$0	$0	$0	$0
Administrative Professionals	$0	$0	$0	$0	$0
Technicians	$0	$2,361	$4,508	$4,504	$0
Crafts	$0	$0	$0	$0	$0
Clerical/Secretarial	$0	$0	$0	$0	$0
Total Direct Labor	$3,959	$7,825	$17,204	$17,200	$2,210
3. Overhead					
Organization OverHead	$1,182	$4,714	$10,029	$10,026	$980
Program Dev. and Mgmt	$330	$1,235	$2,838	$2,825	$206
Total Overhead	$1,512	$5,949	$12,868	$12,851	$1,186
4. Travel					
Transportation	$0	$0	$0	$0	$0
Substistence	$0	$0	$0	$0	$0
Total Travel	$0	$0	$0	$0	$0
5. Other Direct Costs					
Non-Labor Dir. Costs	$360	$1,333	$2,678	$2,814	$248
Total Other Direct Costs	$360	$1,333	$2,678	$2,814	$248
6. Value Added	$5,830	$15,355	$33,400	$33,503	$3,644
7. Other Indirect Costs	$0	$0	$0	$0	$0
8. Direct Materials					
Miscellaneous Materials	$0	$527	$1,271	$928	$0
SubContract/OHC	$0	$5,935	$15,474	$15,474	$0
Total Direct Materials	$0	$6,462	$16,745	$16,402	$0
9. LDRD	$507	$1,336	$2,906	$2,915	$317
10. Gen. & Admin Exp.	$1,475	$3,885	$8,450	$8,476	$922
11. SubTotal	$7,813	$27,038	$61,501	$61,295	$4,883
12. Service Assessment	$188	$649	$1,476	$1,471	$117
13. Total PNNL Cost	$8,000	$27,687	$62,977	$62,767	$5,000
14. Fed Admin Charge	$0	$0	$0	$0	$0
15. Total COST + FED Admin	$8,000	$27,687	$62,977	$62,767	$5,000

Table 3. (contd)

	FY08				
1. Direct Materials Svc Chgs	Project Management	Neutral & Base-Catalyzed	Heterogeneous Hydrolysis	Performance Assessment Sampling	Data Analysis & Reporting
Procurement Svc Charges	$0	$11	$11	$11	$0
SubContract Admin.	$0	$148	$148	$148	$0
Total Dir. Mat. Svc Chgs	$0	$158	$158	$158	$0
2. Direct Labor					
Research Scientist/Eng	$1,490	$2,733	$2,964	$2,964	$4,431
Science & Engineering Associates	$0	$0	$0	$0	$0
Administrative Professionals	$0	$0	$0	$0	$0
Technicians	$0	$1,188	$1,265	$1,265	$0
Crafts	$0	$0	$0	$0	$0
Clerical/Secretarial	$0	$0	$0	$0	$0
Total Direct Labor	$1,490	$3,922	$4,229	$4,229	$4,431
3. Overhead					
Organization OverHead	$444	$2,377	$2,546	$2,546	$1,964
Program Dev. and Mgmt	$124	$676	$707	$707	$413
Total Overhead	$568	$3,053	$3,253	$3,253	$2,376
4. Travel					
Transportation	$0	$0	$0	$0	$0
Substistence	$0	$0	$0	$0	$0
Total Travel	$0	$0	$0	$0	$0
5. Other Direct Costs					
Non-Labor Dir. Costs	$131	$582	$624	$624	$481
Total Other Direct Costs	$131	$582	$624	$624	$481
6. Value Added	$2,189	$7,715	$8,264	$8,264	$7,288
7. Other Indirect Costs	$0	$0	$0	$0	$0
8. Direct Materials					
Miscellaneous Materials	$0	$529	$529	$529	$0
SubContract/OHC	$0	$3,697	$3,691	$3,691	$0
Total Direct Materials	$0	$4,226	$4,220	$4,220	$0
9. LDRD	$190	$671	$719	$719	$634
10. Gen. & Admin Exp.	$554	$1,952	$2,091	$2,091	$1,844
11. SubTotal	$2,933	$14,565	$15,293	$15,293	$9,766
12. Service Assessment	$70	$350	$367	$367	$234
13. Total PNNL Cost	$3,003	$14,914	$15,660	$15,660	$10,000
14. Fed Admin Charge	$0	$0	$0	$0	$0
15. Total COST + FED Admin	$3,003	$14,914	$15,660	$15,660	$10,000

7.0 References

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Appendix A

Scientific Basis for Proposed Work

Appendix A

Scientific Basis for Proposed Work

A.1 Abiotic Degradation Mechanisms Relevant for Carbon Tetrachloride

This section focuses on the scientific understanding of hydrolysis and other abiotic degradation mechanisms relevant for carbon tetrachloride. Previous fate and transport studies have demonstrated that the abiotic degradation of carbon tetrachloride and partitioning to aquifer sediments are the two parameters where uncertainty in the parameter values most significantly affect the fate and transport of carbon tetrachloride (Truex et al. 2001; Bergeron and Cole 2005). In these studies, both Monte Carlo simulations for one-dimensional transport modeling and directed studies using a three-dimensional model concluded that the range of potential abiotic degradation rates (i.e., homogeneous hydrolysis) includes values that would result in attenuation of the carbon tetrachloride plume such that natural attenuation would be an important component of the remedy along with active remediation. However, the range also includes values that do not significantly attenuate the plume. Based on this analysis, studies of abiotic degradation mechanisms and carbon tetrachloride partitioning have been initiated with additional work proposed herein.

A.2 Homogeneous Hydrolysis of Chloroform

The literature on homogeneous hydrolysis rates of chloroform contains conflicting data. For example, a room-temperature sealed-ampule study of chloroform hydrolysis (Dilling et al. 1975) yielded a half-life of 1.25 years. In contrast, the extrapolated high-temperature (100°C–150°C) data of Fells and Moelwyn-Hughes (1958, 1959) for chloroform show a half-life of 3500 years at 25°C. Jeffers et al. (1989) reported a half-life for chloroform of 1850 years at pH 7 and 25°C, based on data collected at 50°C–170°C.

Dilling et al. (1975) stated that the faster rates obtained at 25°C possibly result from different mechanisms operating at low temperature than at the elevated temperature. This possibility is supported by the failure of the Fells and Moelwyn-Hughes (1958, 1959) data to be adequately described by the standard two-constant Arrhenius equation. Other differences in the high- and low-temperature data sets are 1) that a large headspace (49%–72% of the total ampule) was used in the low-temperature work, whereas Jeffers et al. (1989) restricted headspace to the minimum needed to prevent ampule breakage (about 5%), and 2) initial concentrations were 1 ppm in the low-temperature work, and 1125 ppm for the Moelwyn-Hughes high-temperature data (1958, 1959). It is unclear what the initial chloroform concentration was in the Jeffers et al. (1989) work at high temperature, although it was probably between 1% and 10% of aqueous saturation (i.e., 82–820 ppm). The low initial concentration in the Dilling et al. (1975) work suggests that microbial action could be a possible mechanism in the degradation. No pH data were reported, and it could be that the vials used by Dilling et al. (1975) were from a soft glass that dissolved readily and thereby increased the pH well into the alkaline region. The large headspace used, which more closely simulates actual groundwater conditions, could provide sufficient oxygen for oxidation of chloroform and methylene chloride, and sufficient volume for the CO_2(g) produced by hydrolysis to accumulate without exerting chemical backpressure on the reaction. This latter possibility assumes hydrolysis is a reversible reaction, which may not be the case.

A.3 Heterogeneous Hydrolysis of Carbon Tetrachloride and Chloroform

To our knowledge, no studies have been made of heterogeneous effects on hydrolysis of either carbon tetrachloride or chloroform. A limited body of work exists for other organic compounds. For example, Jeffers et al. (1994) attempted to measure the possible effect of mineral surfaces on hydrolysis rate of trichloroethane, trichloroethene, and perchloroethene, and found the rates for these compounds unchanged, even in the presence of sulfide minerals. Haag and Mill (1988) saw a possible heterogeneous effect on hydrolysis rate of 1,1,2,2-tetrachloroethane in contact with montmorillonite clay at 40°C, but no effect for this compound in contact with a subsurface sediment. Only one data point was reported for the clay and the results were obscured by a change in pH of the clay system during the experiment. Haag and Mill (1988) did see a clear effect of the sediment on hydrolysis of styrene oxide, an epoxide compound. Deeley et al. (1991) studied the transformation of 1,2-dibromo-3-chloropropane (a soil fumigant) at concentration of 1 ppm in a sediment slurry and saw no significant effect of the sediment on hydrolysis rate. In 2000, we contacted Peter Jeffers and Ted Mill, two of the primary researchers in this field. Both individuals thought that further laboratory work to determine whether heterogeneous effects occurred with Hanford sediments under ambient conditions would be a good idea before making a remediation decision.

The possible mechanism by which heterogeneous hydrolysis differs from homogeneous hydrolysis is associated with the sorption of carbon tetrachloride or chloroform to the solid phase. By analogy to heterogeneous catalysis theory, sorption can increase the hydrolysis rate by the immediate release of energy that occurs when the surface complex forms. This energy temporarily raises the local temperature and effectively lowers the activation energy for the reaction. If the reaction does not occur at the time of sorption, the subsequent opportunities for reaction may be greater or less than if the carbon tetrachloride or chloroform were still in solution. Strain on the sorbed molecule and enhanced levels of hydroxyl ions near the surface (if positively charged) might promote the reaction for chloroform. On the other hand, because sorption may decrease the accessibility of water (or hydroxyl ion) to the carbon tetrachloride or chloroform, the possibility of a favorable molecular collision that would promote the reaction may be less. The relative strength of these three factors (sorption energy, strain, accessibility) is unknown for the system of interest.

We can, however, estimate the maximum possible benefit to be derived if we focus on the effect of sorption energy alone. Sorption energies for chlorinated hydrocarbons (trichloroethene and chloroform) onto organic surfaces have been estimated to be about 33 kJ mol-1 (Alben et al. 1988). If we assume a value of 33 kJ mol-1 as the sorption energy for carbon tetrachloride and assume further that this energy decreases the activation energy for hydrolysis by the same amount (i.e., from 113 kJ mol-1 to 80 kJ mol-1), we can calculate the rate constant for heterogeneous sorption using the Arrhenius expression. However, first we need to calibrate the pre-exponential factor (A). This is done by assuming that the heterogeneous rate observed is 5% of the homogeneous rate observed at the lowest temperature reported (70°C, Jeffers et al. 1989) and calculating A as the quotient of the rate constant and the exponential term in the Arrhenius expression. When this is done, a value for the heterogeneous rate constant of 1.2×10^{-7} min-1 is obtained at 17°C.

To help visualize the maximum possible heterogeneous benefit (i.e., assuming 100% sorption), we have created an Arrhenius plot showing the homogeneous data of Jeffers et al. (1996) extrapolated to lower temperatures together with the predicted line for heterogeneous kinetics assuming no heterogeneous effect above 80°C (Figure A.1). At a temperature of 17°C, the homogeneous half-life for carbon tetrachloride is about 138 years, whereas the maximum heterogeneous half-life is only 11.3 years, a twelve-fold increase in rate.

In reality sorption will not be 100%, and so we need to determine the relative fractions of carbon tetrachloride that are sorbed or in solution. This can be done for a 1000 ppb carbon tetrachloride solution using a representative K_d value of 0.12 (Truex et al. 2001) and assuming 15% porosity and a particle density of 2.65 kg L-1 for the sediment. With these values, we calculate that 35% of the carbon tetrachloride is in solution and 65% is sorbed to the surface. Finally, we calculate an observed rate constant assuming proportional contributions from the homogeneous and heterogeneous fractions of the carbon tetrachloride and obtain 7.9×10^{-8} min-1. This maximum estimated value is roughly eight times faster than the homogeneous rate of 9.5×10^{-9} min-1 calculated from Jeffers et al. (1989). We have indicated this value by a star symbol in Figure A.1. Clearly, heterogeneous effects have the potential to be important and increasingly helpful at lower temperatures.

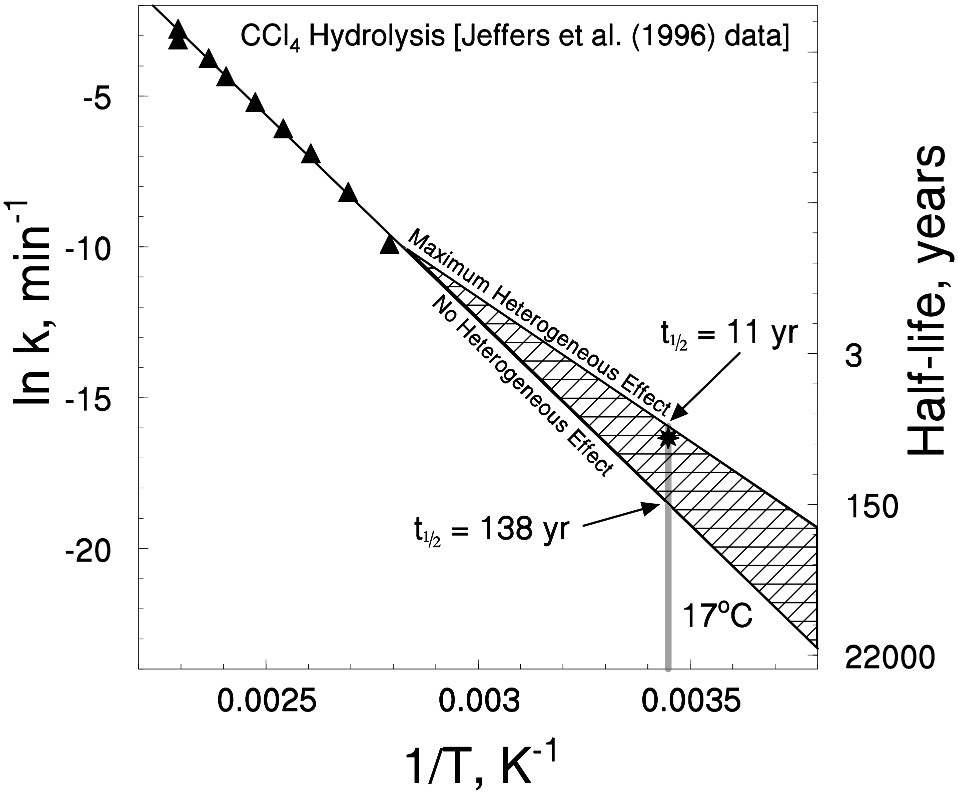

Figure A.1. Arrhenius Plot Showing Homogeneous Hydrolysis Rate Data Collected at High Temperatures Extrapolated to Lower Temperatures and the Maximum Estimated Heterogeneous Hydrolysis Rate Assuming 100% Adsorption and no Heterogeneous Effect Above 80°C. The shaded area indicates where heterogeneous effects might be expected and the star symbol shows the maximum heterogeneous rate predicted for a Hanford sediment in contact with a 1000 ppb carbon tetrachloride solution at 17°C (K_d of 0.12 L kg-1).

A.4 References

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Appendix B

Response to Summary Comments from Supplemental Columbia River Activities Peer Review

Appendix B

Response to Summary Comments from Supplemental Columbia River Activities Peer Review

Responses to Supplemental Columbia River Protection Activities Peer Review

Proposal Title: Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions

B.1 Summary Evaluation

The panel supports the proposed study. There was general consensus the proposal is based on appropriate and valid science and has merit to address the carbon tetrachloride plume. Moreover, the study would fill an existing science gap at Hanford and complements and leverages the current homogenous hydrolysis study. For a large plume like carbon tetrachloride at Hanford, hydrolysis and similar degradation processes that are traditionally neglected may be significant in limiting contaminant migration.

Reductive processes that dominate attenuation at many sites are not operative at Hanford due the presence of oxygen and nitrate in the groundwater. In this case, hydrolysis rates of the chloromethanes, while slow, are likely to be a primary determinant in the potential for Columbia River impacts. The current remediation technology is soil vapor extraction and limited groundwater pump and treat. The proposed research is a key step in developing an overarching and long-term plan for carbon tetrachloride and related contaminants at Hanford. Some technical issues/recommendations were identified by the panel, which should be considered by the investigators and the U.S. Department of Energy (DOE) as the research plan is finalized and the work implemented. These concerns were primarily associated with the type(s) of solids used in the heterogeneous studies, the timing and sensitivity of the analysis, the total length of time needed for the study, the quality assurance (QA) and equivalency requirements associated with a multi year study, etc.

B.2 Technical Basis of the Proposal

In general, the panel believes the proposal is based on appropriate and valid science. The panel provided some specific technical issues for consideration. These are summarized below along with an identification of reviewers who provided detailed topical comments and recommendations. The researchers are strongly encouraged to read the relevant individual reviews as they finalize their plans.

1. *Consider clarifying the linkage with historical and ongoing work – expanding the discussion of how this study builds on the previous study of the homogeneous hydrolysis of chloroform (CF). (Reviewers 2, 6 and 7)*

Response: The main point to clarify is that no one has collected data for the neutral homogeneous hydrolysis rate of chloroform at temperatures within 120°C of groundwater temperatures (ca. 15°C–20°C). As a result all hydrolysis data are extrapolated well beyond the zone where most statisticians would be comfortable and have correspondingly wide confidence intervals associated with them. Moreover, no one (aside from the ongoing study of carbon tetrachloride that has just started) has looked the possibility of heterogeneous catalysis of hydrolysis for chloroform (or carbon tetrachloride). This work, therefore, builds our confidence in the homogeneous rates by making the zone of extrapolation smaller and the associated window of uncertainty, narrower. And, it explores a possible catalytic effect that could have a large impact on how we decide to remediate the existing plume.

2. *Consider using real samples for heterogeneous experiments, including both sediments and groundwater. Existing sediment cores from the field should be used as the basis for selecting the minerals to use in the heterogeneous hydrolysis tasks. The basis for the selected solid materials to be tested needs to be carefully thought out and documented. The selection criteria for the sediments and brief justification should be provided to DOE. (Reviewers 1, 2, 3, 6 and 7)*

Response: We agree with respect to the sediment and groundwater samples (as indicated in the next response below). Further below we have outlined how we plan to identify the minerals to be used. Our plan is to use a fine-grained sediment from the uncontaminated zone down-gradient from the ZP-1 plume, as this will have more reactive surface area per unit mass relative to coarser portions of the formation and be highly relevant to the eventual degradation pathway of the plume. Typically, the surface area of particles larger than silt size can be ignored from a chemical reactivity perspective.

3. *Sediment and groundwater samples need to be identified by their composition and where they were obtained. Consideration should be given to concerns regarding whether real sediment and groundwater samples can be considered representative of Hanford. (All Reviewers)*

Response: We agree with the reviewers. The sediment and groundwater will be collected from an uncontaminated zone downgradient from the ZP-1 plume (i.e., where the plume is likely to head in the coming years). No single sample or set of samples, however, can adequately represent all of Hanford! If the latter were required, then a project of much larger scope would be needed.

4. *Since a significant hydrolysis reaction could occur at ambient temperature, the proposal should consider inclusion of (or shifting to) a test point of 15 degrees centigrade, which is closer to the ambient temperature. (Reviewers 1,5 and 6)*

Response: We have looked at groundwater sampling records for the ZP-1 plume area over a year of sampling. These show an average groundwater temperature of about 19°C with a standard deviation of less than 2°C. We think that the error in extrapolation of hydrolysis rates from a dataset of 20°C–70°C relative to that for one from 15°C–70°C is small, and probably not worth the additional effort.

5. *Address mineralogy concerns:*

   Milling and grinding sediments could produce reactive mineral states and influence test results. If the reactive minerals are coated on the sediment particles than typical assumptions and interpretation associated with ground sediment might underestimate attenuation – if the grinding exposed active reaction sites than the interpretation might overestimate attenuation. (Reviewers 1, 4, 5, and 6)

Response: We agree with the reviewers that grinding will produce a more active surface. However, the options are fairly limited if one wants to identify a particular mineral that leads to possible heterogeneous effects. We can take different size fractions of the sediment that will have somewhat different mineralogy, but then reactive surface area becomes a major factor. It all depends on the amount of reactivity seen. If a particular ground mineral surface is very reactive, then there is a possibility of using a low-surface area unground mineral in an experiment such as the ones we propose. Otherwise, we are left with picking silt-sized grains of minerals from a sediment, one by one, until we have enough to perform an experiment, and that is not practical given the funding and time-frame of the project. If heterogeneous effects are present, then we will need to cross the bridge as to how to provide a predictive capability that truly represents what occurs in the subsurface. Such an enterprise, however, is beyond the scope of the present project.

> *Consider conducting some bulk analysis of the raw sediment (looking for mineralogical distribution, coatings, etc.) as an adjunct to the microcosms. (Reviewers 1 and 6)*

Response: We have added some characterization activities to our work plan to ensure that we know some of the most important properties of the solid phases with which we will work. As the sediment is one of these solids, some information about mineral distribution and presence of oxide coatings will be collected. We will leverage our work with a recently funded ERSP project (Richelle Allen-King, PI) whose aim is to identify the impact of different types of sediments on reductive transformations of CT in the same Hanford sediments of the 200 West Area, ZP-1.

> *Identify the mineral powders that will be used in the study. The identification should be based on a clearly stated conceptual model and test specific hypotheses that will be used when modeling plume migration and stabilization. (All Reviewers)*

Response: We indicated in the introduction that clays, zeolites, feldspars, and iron oxides were likely candidate classes of minerals that need to be examined. Our approach will be to examine the mineralogy (and its distribution such as the presence of coatings) of uncontaminated sediment obtained from the vicinity of the ZP-1 plume, and from that analysis decide which four minerals are the most representative of the sediment. We cannot at this point in time say definitively what those minerals will be.

> *Avoid using the terms "minerals" and "sediments" interchangeably. (Reviewer 1)*

Response: We did use these in the same sentence, but not interchangeably, as both were sample types to be included in our experimentation. We apologize if the reviewer received a different impression.

6. *Consider possible impacts of other contaminants in the CT plume, resulting from the original waste being a diverse mixture containing inorganic brine, and organic co-contaminants. (Reviewers 6 and 7)*

Response: Our understanding is that there are no co-contaminants in most of the carbon tetrachloride/chloroform plume at Hanford 200 West, ZP-1. To consider the possible impacts of co-contaminants would require a significant change in the scope and funding of this project.

7. *Identify and consider all daughter products that may have been produced by the contamination plume. The presence of daughter products may offset the positive effects of reducing the CT. (Reviewers 3 and 6)*

Response: For pure hydrolysis, the only products are HCl and CO_2, both of which are considered benign. If reduction is also occurring, daughter products such as chloroform, dichloromethane, and even two-C compounds may be seen. The point of using monitored natural attenuation of hydrolysis is to avoid the production of these undesirable products. We are not trying to reduce the carbon tetrachloride and agree that reduction might not be a beneficial approach to the problem.

B.3 Implementation Strategy

1. *The proposed study complements an ongoing study, and is integrated well with current modeling work*

Response: We agree.

2. *Proposal appears to be cost-effective.*

Response: We agree!

3. *Address concerns about the longevity of the proposed study:*

The study will likely take between four to six years to complete. Funding through this program is only provided for two years, so subsequent funding will need to be secured to complete the study. Additional funding may be available, but some tangible progress must be demonstrated after two years.

Given the slow reaction rates at the lower temperatures to be used in the proposed study, determine whether useful data can be obtained within the proposed time frame. (All reviewers)

Response: We agree with the need for tangible progress. In 2 years time, we should be able to narrow the window of uncertainty on hydrolysis rates at lower temperatures for both carbon tetrachloride and chloroform. For carbon tetrachloride, we expect to be able to measure hydrolysis rates all the way to 20°C (see performance metrics response below). Assuming the rate of homogeneous hydrolysis of chloroform is about 46 times slower than that of carbon tetrachloride (Jeffers et al. 1989), we expect to get usable data down to 40°C using the sealed ampules with 0.5 headspace/solution ratio. If heterogeneous effects are present, lower temperatures and an even narrower window can be obtained for groundwater temperatures. Given that existing data for neutral hydrolysis of chloroform (Jeffers et al. 1989) were collected at 140°C and above, the improvement in extrapolated values at 20°C should be significant. If heterogeneous effects are present, data for lower temperatures and an even narrower window of uncertainty can be obtained.

4. *In a multiyear study, issues of detection limits and quality assurance are of paramount importance. These issues should be carefully considered to assure proper sensitivity and detectability as well as to assure that data are usable. (see performance metrics)*

Response: We agree and think that our response in the performance metrics section describes our approach to this issue fully.

B.4 Proposed Performance Metrics

1. *In general, the performance metrics discussed in the proposal seem reasonable and appropriate. The hydrolysis parameters and the 95% confidence interval at 15 degrees centigrade are measurable parameters that will document performance.*

Response: Agreed.

2. *Support using perchloroethene (PCE) as an internal standard to monitor a possible decrease in CF and CT starting concentrations in water over five years. Assuming the same instrument and detector are used for the duration of the study, quality assurance was not described that would identify selective changes in detector response of CF, CT, or PCE. Based on the trend of the change in response, decreases in concentration of CT and CF could be calculated when in fact the concentrations had not changed. To monitor consistency of detector response, a sufficient supply of check samples to contain PCE and either CF or CT should be prepared in glass sealed tubes and stored refrigerated in the dark. The check samples should be analyzed as samples at each sampling period and the calculated concentrations of CT and CF should remain constant over the five years. Need to calculate detection limits to assure proper sensitivity to accurately measure expected changes. (All reviewers)*

Response: The primary analytical method we will use to determine hydrolysis rate will be ion chromatography (for Cl^- ion determination). For this determination, a primary standard is easily prepared that will not degrade over time. That being said, check samples are essential and will be prepared/stored as suggested by the reviewers.

Our current detection limits for Cl^- are on the order of 10 ng mL^{-1}. Starting with a 40 ppm carbon tetrachloride solution, complete hydrolysis would yield 36,900 ng (Cl^-) mL^{-1}. Thus, we should be able to detect a fractional change of 0.00027 in concentration. The predicted homogeneous hydrolysis rate for carbon tetrachloride at 20°C (using the current extrapolated data) suggests that a fractional change in concentration of that size should occur every 20 days (after accounting for the decrease in rate due to a headspace/solution ration of 0.5). This is the worst case for carbon tetrachloride, as heterogeneous effects may speed up the rate. For chloroform, a 40 ppm solution will yield 33,600 ng (Cl^-) mL^{-1} and a fractional change detectability of about 0.00030. The extrapolated homogeneous hydrolysis rate at pH 7 for chloroform at 25°C (Jeffers et al. 1989) suggests that a much longer time (ca. 3.7 years) is needed for a detectable change. So, with chloroform we will not detect a change at the lowest temperatures during the 2-year term of the project unless heterogeneous effects act to speed up the hydrolysis rate.

3. *Consider indicating how the disappearance of the contaminants will be monitored after two to five years.*

Response: Technically, the monitoring will follow the same procedures as used in the first 2 years (i.e., ion chromatography, with GC/MS used to determine degradation pathway). Obviously, additional funding will be needed for this to occur, and the likelihood of obtaining this funding will depend on the quality and usefulness of the data generated in the current project.

B.5 Reference

Jeffers PM, LM Ward, LM Woytowitch, and NL Wolfe. 1989. “Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes, and Propanes.” *Environ. Sci. Techno*l. 23:965-969.

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