Abiotic Degradation Rates for Carbon Tetrachloride and Chloroform: Progress in FY 2008

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October 2008

Pacific Northwest
NATIONAL LABORATORY

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[1] The Research Foundation of the State University of New York, Cortland, New York.

Abstract

This is a letter report summarizing work performed in FY2008 to determine the rates of carbon tetrachloride hydrolysis at temperatures close to actual groundwater temperatures. The report describes the project, the methodology, and the results obtained since the project's inception in FY2006. Measurements of hydrolysis rates in homogeneous solution have been completed for temperatures of 70°C through 40°C, with additional data available at 30°C and 20°C. These results show no difference between the rates in deionized H2O and in filter-sterilized Hanford-Site groundwater. Moreover, the rates measured are 2-3 times slower than predicted from the open literature. Measurements of rates involving sterile suspensions of Hanford-Site sediment in Hanford-Site groundwater, however, show faster hydrolysis at temperatures below 40°C. Extrapolation of the current data available suggests a six-fold increase in rate would be expected at groundwater temperature of 16°C due to the presence of the sediment. This result translates into a 78-year half-life, rather than the 470-680 year half-life that would be predicted from rate determinations in homogeneous solution. The hydrolysis rate data at 20°C, in contrast to those at higher temperatures, are preliminary and have low statistical power. While significant ($p < 0.05$) differences between the heterogeneous and homogeneous systems are seen at 30°C, the results at 20°C are not statistically significant at this level due to limited data and the very slow nature of the reaction. More time is needed to collect data at these low temperatures to improve the statistical power of our observation. Given the critical need for hydrolysis rate data at temperatures relevant to groundwater systems, we have three recommendations for future work. First, we recommend a continuation of the sampling and analysis of the remaining long-term sealed-ampule experiments described in this report. These are primarily 20°C and 30°C experiments. The data at 20°C, which are most germane to the groundwater environment, will likely take two more years before they are complete. Second, due to the importance of heterogeneous effects, we recommend the continuation of sampling and analysis for a similar set of experiments looking at hydrolysis rates of CT and CF in contact with individual minerals (montmorillonite, kaolinite, albite, and muscovite) or Hanford-Site sediment, and, for CF, in homogeneous solutions. These experiments were set up under a separate project funded by a congressional earmark (EM-22) for which funding expired at the end of FY08. Third, we strongly recommend development of a ^{13}C/^{12}C isotope ratio mass spectrometry (IRMS) approach for determination of hydrolysis rates at groundwater temperatures and relevant CT and CF concentrations. The technique is sensitive enough that we expect to be able to shorten the time required for a rate-constant determination by 20-fold. Thus, a 5-year experiment conducted by the sealed-ampule approach could be shortened to 3 months by the IRMS approach. This sensitivity also would allow the IRMS technique to be used to follow hydrolysis rates at concentrations found in groundwater plumes at Hanford.

Abbreviations

CF   chloroform
CT   carbon tetrachloride
DOE   U.S. Department of Energy
IRMS   isotope ratio mass spectrometry
PNNL   Pacific Northwest National Laboratory
RSD   relative standard deviation
SUNY–Cortland State University of New York at Cortland
ZHR   zero-headspace reactor

Contents

1.0   Introduction

1.1   Rationale

Between 1955 and 1973, an estimated 920,000 kg of carbon tetrachloride (CT) were discharged to the soil in the 200 West Area of the Hanford Site as part of the plutonium production process (Oostrom et al., 2007). Of this amount, some CT reached the groundwater more than 70 m below the ground surface and formed a plume of 10 km^2 extent. Recent data show that the CT plume extends to a depth of at least 60 m below the water table. Some CT has been degraded either by the original process or subsequent transformations in the subsurface to form a co-existing chloroform (CF) plume.

Upcoming remediation decisions will rely on an improved conceptual model of the plume as well as mechanistic information concerning the fate and transport of CT/CF. A key aspect of these decisions will be to determine the relative sizes of the efforts devoted to active remediation and natural attenuation in order to stabilize the plume. Of the possible natural-attenuation mechanisms, biodegradation is not likely to contribute significantly (Truex et al., 2001), and mechanisms such as dispersion, dilution, and sorption to Hanford-Site sediments have been the focus of previous field and modeling efforts (e.g., Riley et al. 2005). In contrast, abiotic-degradation processes such as hydrolysis and reduction, which are likely to contribute significantly to natural attenuation (Truex et al., 2001), are not well understood or quantified. The work in this project is designed to partly bridge that gap by determining the mechanisms and rates associated with hydrolysis.

Current estimates of chlorinated-methane hydrolysis rates are based on studies conducted at high temperatures (typically 70-150°C) and extrapolated using the Arrhenius equation to ambient conditions. Additional error is added by the assumption that the Arrhenius prefactor and the activation energy for the reaction do not change with temperature. Slight curvature in the Arrhenius plot of Jeffers et al. (1996) for carbon tetrachloride (CT), however, suggests that these two parameters do indeed change with temperature and that the decrease in hydrolysis rate with temperature is more than that predicted by the linear Arrhenius equation (Fig. 1). When the prefactor "A" in this equation is allowed to vary with temperature as suggested by activated-complex theory, hydrolysis half-lives of 350-500 years are predicted at 16°C, two to three times longer than predicted by the simple Arrhenius equation. An empirical extrapolation using a quadratic polynomial expression to fit the data predicts a half-life at 16°C of nearly 20,000 years. Clearly, the use of data extrapolated from higher temperatures to estimate hydrolysis rates at groundwater temperatures injects considerable uncertainty into any attempt to determine the role of abiotic processes in CT degradation and frustrates the development and design of possible remedies. To resolve this situation, collection of hydrolysis rate data at temperatures at or near actual groundwater temperatures is needed. Because the hydrolysis rates are very slow at low temperatures, adequate resolution of
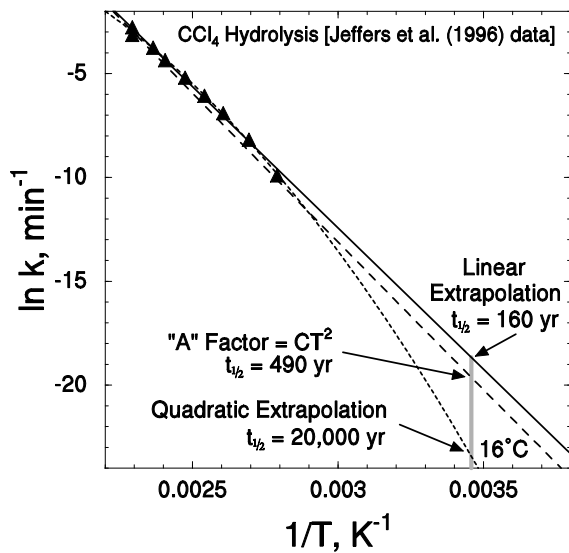

Figure 1. Arrhenius plot for homogeneous hydrolysis of CCl₄ showing three extrapolations from the high temperature data of Jeffers et al. (1996) to groundwater temperatures of 16°C.

1

the issue requires a lengthy experiment (as long as 5 years), extremely accurate sampling and analytical procedures, control of temperature and microbial populations, adequate headspace in the vials to minimize pressure effects, and a large number of replicates. Not surprisingly, the combination of these requirements has inhibited the collection of these data at ambient temperatures heretofore.

1.2   Project Goals

The goals of this project are to

1) determine the homogeneous rates of hydrolysis for CT in deionized water and Hanford groundwater at six discrete temperatures from 20°C to 70°C,
2) determine the Arrhenius parameters (i.e., activation energy and prefactor) for hydrolysis of CT in aqueous systems using the hydrolysis rate data collected at temperatures of 20°C to 70°C together with previously published data, thus allowing highly accurate interpolated estimates of hydrolysis rate at any temperature in the 20°-150°C range and reasonable extrapolation to groundwater temperatures, and
3) determine whether heterogeneous effects on CT hydrolysis might be important by conducting exploratory tests using a suspension of fine-grained Hanford-Site sediment in Hanford groundwater.

1.3   Project Organization

The project manager is Jim Amonette (PNNL), who also serves as co-PI with Peter Jeffers (SUNY-Cortland) and Mike Truex (PNNL). Work on the project is being conducted in two laboratories: the Environmental Molecular Sciences Laboratory at PNNL, and the Chemistry Department at SUNY-Cortland. At PNNL, work focuses on determinations of hydrolysis rates in deionized water, Hanford groundwater, and suspensions of Hanford-Site sediment in groundwater using ampules with a headspace:liquid ratio of 1:2. At SUNY-Cortland, work focuses on hydrolysis-rate determinations in deionized water and groundwater using minimal-headspace ampules (headspace:liquid ratio of about 1:50) and a zero-headspace reactor. Work at SUNY-Cortland also includes direct determinations of aqueous:vapor partition coefficients for CT using a specially-built reactor.

2.0   Experimental Approach and Method Development

Our approach is designed to succeed in the shortest time possible while producing a robust dataset that will withstand the critical scrutiny of scientists, decision-makers, and stakeholders.

2.1   Experimental Design

The overall experimental design involves collection of data at *six temperatures* covering the range of 20-70 °C. Samples are incubated under one of *three environments* (sterile DI water, sterile filtered Hanford 200-Area groundwater, or sterile Hanford 200-Area sediment in 200-Area groundwater), at one of *two concentrations* (40, 400 ppm), for periods of up to five years. We conduct *five replicate analyses* for each treatment combination at each of *ten times* during the experiment. Thus, the total number of experimental units at PNNL is 6x3x2x5x10 = 1800. Corollary experiments are conducted at SUNY-Cortland for the DI and groundwater environments and typically involve triplicate analyses for each treatment combination/time period.

2.2   Groundwater and Sediment

Uncontaminated Hanford groundwater was obtained from Well 699-49-100C located near the Yakima barricade west and upgradient of the 200-West Area at the Hanford Site. The sample # B1JX90 (SAF# X06-043) was collected on 12 July 2006. Water from this well has been used by the Hanford groundwater monitoring project for background values for a number of years. Uncontaminated sediment from the Ringold Lower Mud formation at Hanford was a silt loam (22% clay, 78% silt) obtained from Borehole 299-W15-46, SAF#F03-018, SAMP# B19NK8. The sample was collected on 4 Jan 2005 at 216-Z-9/C3426 from a depth of 421.5'-423.5' using a split-spoon liner.

2.3   Determination of Hydrolysis Rates

2.3.1 PNNL Methods. At PNNL, a stock solution saturated with CT is prepared by adding 8 ml of HPLC-grade CT (>99.9% pure, Sigma-Aldrich, 27 0652) to 1 L deionized H_2O in a borosilicate glass bottle containing ten glass beads. The mixture is shaken continuously on an orbital shaker at 150 rpm for several weeks before using. The nominal concentration of CT in this stock solution is about 800 mg L^{-1} (i.e, the limit of solubility).

Starting solutions for hydrolysis determinations are prepared in 1.2-L PTFE gas sampling bags (Alltech 41004, Deerfield, IL). The appropriate masses of CT stock solution and deionized water are filter-sterilized (Anotop 25, Whatman) and added to the sampling bag using a sterile glass syringe driven by a syringe pump. Also, 10 uL of neat perchloroethene (PCE), which has an hydrolysis half-life of 10^9 years (Jeffers et al. 1989), is added to serve as an internal standard during gas chromatographic (GC) analyses. Some of the water is added initially and the headspace in the bag eliminated before the CT stock solution and PCE are added. A typical total volume in the bag is about 800 mL and initial CT concentrations are nominally 40 or 400 mg L^{-1}. After addition, the contents of the bag are mixed by gently squeezing the bag. Then the outlet on the bag is attached to the inlet of an automatic dispenser designed for organic liquids (Dispensette® Organic, BrandTech Scientific, Essex, CT) and the contents dispensed through a large-bore stainless-steel needle into ampules for immediate sealing.
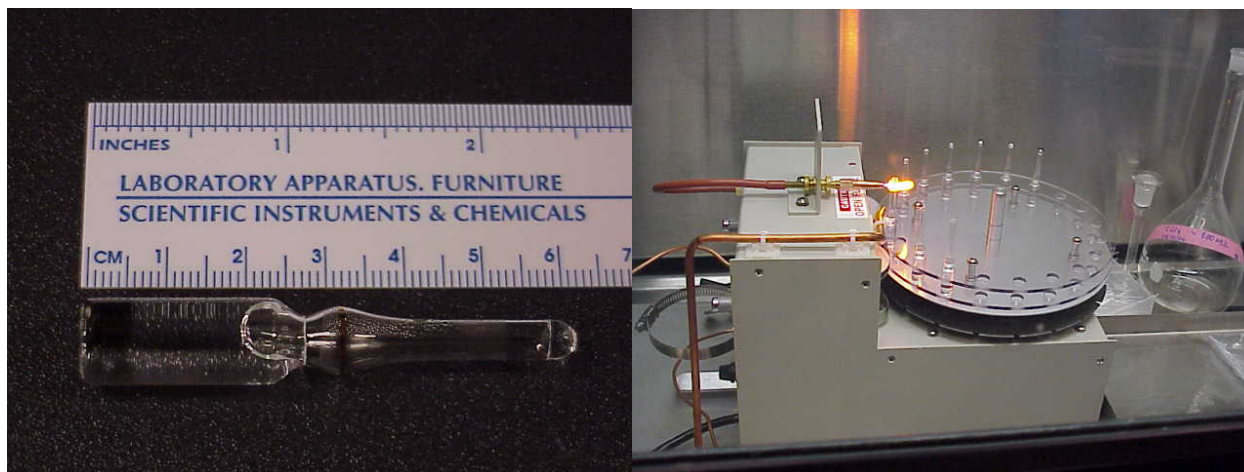
Figure 2. Ampule (left) and automatic ampule sealer (right) used for PNNL hydrolysis experiments.

The hydrolysis experiments are conducted in 1-mL (nominal volume) glass ampules (Figure 2 left, Wheaton 176772, Millville, NJ). These ampules typically have an internal volume of 2.3 ml when sealed. We add 1.6 ml of aqueous sample to the ampule, leaving 0.7 ml as headspace. The ampules are sealed within 15 s of sample addition using an automatic ampule sealer (Figure 2 right, Ampulmatic Model 290 001, Bioscience, Inc., Bethlehem, PA).

For each incubation temperature, 84 ampules are prepared. Seventy of these are incubated at the desired temperature and sampled in batches of seven after various periods to determine hydrolysis rate. The first batch is sampled immediately after ampule sealing and defines the starting conditions for the experiment (e.g., some hydrolysis can occur during the ampule-sealing process due to the high temperatures involved). The remaining 14 ampules are controls. Seven are incubated at 100°C until hydrolysis is complete and then analyzed to determine the *actual* starting concentration of CCl_4 in the ampules. The other seven are stored at 4°C where
hydrolysis rates are negligible. These seven serve as reference points for the initial conditions in case any questions arise during the course of the experiment.

During the ampule-preparation process, eight of the 84 ampules are selected at regularly spaced intervals to provide data for the estimation of headspace volume (this is done by weighing the empty ampule and the same ampule after filling and sealing). After incubation, but before the ampules are opened during the sampling process, the ampules are reweighed to verify no leakage, and their headspace is determined by a differential density approach. A syringe large enough to contain the ampule is filled with water of known density and weighed. Some of the water is then displaced by the sealed ampule (the total volume within the syringe remains the same with no air bubbles) and the syringe with ampule is reweighed. From these data and the physical properties of the solutions and glass, the headspace within the ampule is calculated by

$$V_{HS} = (m^A_{tot} - m^B_{tot} + m_{Amp+CT})/\rho_{H2O} - (m_{Amp}/\rho_{Amp}) - (m_{CTsoln}/\rho_{CTsoln}) \qquad [1]$$

where m^A_{tot} = mass of syringe filled with H_2O, m^B_{tot} = mass of syringe filled with sealed ampule and H_2O, m_{Amp+CT} = mass of filled ampule, ρ_{H2O} = density of water, m_{Amp} = mass of empty ampule, ρ_{Amp} = density of glass in ampule, m_{CTsoln} = mass of solution in ampule, and ρ_{CTsoln} = density of solution in ampule.

The 70 ampules for hydrolysis measurement are arranged in labeled metal racks (Figure 3 left) and incubated at the desired temperature using an air-flow incubator (Figure 3 right, Incumax IC 150 or IC

Figure 3. Set of ampules in rack (top left) ready for insertion into incubator (bottom left), and incubator array used in PNNL experiments (right).

150R, Amerex Instruments, Lafayette, CA). Temperature inside each incubator is continuously measured by two thermocouples located near the top and bottom of the incubator volume and recorded on a datalogger (CR3000, Campbell Scientific, Logan, UT). Thermocouples were calibrated initially using a NIST-certified platinum-resistance thermometer (Hart Scientific 1502A, American Forks, UT).

After appropriate periods whose length depends on the expected hydrolysis rate and the sensitivity of our analytical determinations, seven samples are removed from the incubator and the hydrolysis reaction quenched by storage in a 4°C refrigerator. When convenient for analysis, five samples from each time period are opened and their contents transferred to pre-cleaned glass ion chromatography (IC) vials. The pre-cleaning procedure to remove traces of chloride from the IC vials involves soaking them in deionized H_2O for several days with two changes of H_2O during the first day, and one change on each subsequent day. The transferred samples remain at 4°C until IC analysis. If the expected levels of the analyte (chloride ion) are greater than 100 mg L^{-1} then 5x dilutions with deionized H_2O are made from these vials prior to analysis. Otherwise, the vials are analyzed without dilution. Chloride concentrations are determined by ion chromatography (Dionex DX-500, AS11-HC column, suppressed conductivity detection). The remaining two samples from each time period are reserved for GC analysis to verify that only hydrolysis reactions occurred (e.g., reduction would yield some chloroform as a product, which is easily detected by GC methods).

2.3.2 SUNY-Cortland Methods. At SUNY-Cortland, the same general approach is used as at PNNL (i.e., hydrolysis in sealed glass container at temperatures in the 20°-70°C range). Differences are found, however, in the type of container, the headspace:liquid ratio, and in the type of incubator. These measurements utilized two water baths controlled with mercury sensors and electronic relays; they were

easily adjusted to desired temperatures and were stable within 0.1 degree for intervals as long as a month (the longest duration of the actual measurements). Temperatures were measured with mercury thermometers reading to 0.1 degree and the calibration was checked with ice/DI water.

Early experiments were conducted using sealed bulbs made from borosilicate glass tubing. The bulbs were drawn from 8-mm od tubing and typically had a volume of about 1 mL with a void volume of 0.04 – 0.1 mL at 20°C. At high temperature, 70°C, the void volume was reduced to 0.02 – 0.08 mL (value determined both by calculation and measurement). A problem that became apparent early in the work was the appearance of measurable Cl⁻ in t = 0 bulbs, due to inadvertent heating of the solution during the sealing process. Re-design of the bulbs reduced this problem, but failed to eliminate it. A second problem observed in an early bulb experiment at 60°C was the clear evidence of microbial activity. This problem was solved by treating all glassware and other implements that would touch the solution by heating at 120°C overnight, and wearing surgical gloves for bulb filling. A third problem was associated with determination of the appropriate correction to the observed rate constant to account for partitioning of CT between liquid and headspace. The variable headspace in these bulbs and the consequential need to measure headspace on each and every bulb made corrections for CT partitioning tedious at best and added considerable uncertainty to the data, particularly at the higher temperatures.

To avoid the problems with premature hydrolysis and uncertain headspace, a zero-headspace reactor (ZHR), was designed, fabricated, and used with significant success in these studies. The body of the ZHR (Figure 4 top) is a 10-cm length of 20-mm Pyrex® tubing with a10-cm length of 2-mm id Pyrex® capillary at one end and a 25-cm length of 8-mm od Pyrex® tubing at the other end. The capillary is flared at the end to fit inside a ¼ inch Swagelok® fitting and affords a glass-to-septum (10-mm GC) seal. The 8-mm tubing is bent in a U and terminates in a 2-mm Teflon® stopcock with a 2 cm by 10 mm Pyrex® reservoir at the top which extends slightly beyond the capillary end. The reactor is filled using a 50-mL glass syringe with a long wide-bore needle until the solution just spills out past the loosened Swagelok® nut which is then secured. The ZHR is placed into a water thermostat bath with only the ends above water and the stopcock remains open until the solution is temperature equilibrated. Samples are

Figure 4. Zero-headspace reactor (top) and apparatus for determination of liquid-vapor partition coefficients (bottom) fabricated and used for hydrolysis experiments at SUNY-Cortland.

drawn into a 1-mL glass syringe fitted with a 15-cm 17-gauge needle that extends to the middle of the reactor body. The stopcock is opened for the sampling process and fresh reaction mix is placed in the reservoir above the stopcock. Typically, 0.2–0.3 mL of solution is withdrawn for analysis, thus a run totaling 10 samplings drains far less solution than is contained in the 8-mm feed tube, while the very narrow gauge sampling needle causes little mixing in the capillary sampling arm.

The ZHR and all associated glassware, syringes, and needles are heat sterilized before use. The deionized water is boiled and sparged with a flow of He to remove dissolved air. This prevents the formation of air bubbles inside the reactor to which reactant could partition during a run and is an important precaution to take at all temperatures above 40°C.

An essential quantity in calculating the rate constant is the initial concentration of reactant. For experiments in deionized water this value can be measured by complete hydrolysis of the reactor solution at the end of a run, measuring the total chloride ion liberated. Initially, with CCl_4, about 1 mL of solution was withdrawn from the reactor, injected into a 1.2-mL bulb drawn from 8-mm Pyrex® tubing, the bulb was then quickly flame sealed and placed in a 130°C oven for about 30 hr. CCl_4 has a half-life of about 2 hr at 130°C, so hydrolysis should have been complete. The bulb was opened and the solution quantitatively diluted to a range appropriate for IC analysis. A recent significant improvement has been to do the dilution prior to hydrolysis by drawing 7-cm long bulbs from 12-mm Pyrex® tubing, adding a weighed amount of DI water, then injecting about 0.3-0.4 mL solution with the sampling syringe, carefully keeping the needle tip near the bottom of the bulb, then quickly flame sealing and re-weighing to determine the dilution factor. The revised process allows very little opportunity for reactant to diffuse out of solution before the bulb is sealed, and results in very close agreement on concentration with duplicate samples.

2.3.3   Calculation of Hydrolysis Rate Constant, Reaction Half-Life, and Activation Energy.

The hydrolysis of CT follows the overall reaction

$$CCl_4 + 2\ H_2O \rightarrow 2\ CO_2 + 4\ H^+ + 4\ Cl^-. \quad [2]$$

The rate law for this reaction is

$$-d[CCl_4]/dt = (1/4)d[Cl^-]/dt = k[CCl_4] \quad [3]$$

which, upon integration yields

$$[Cl^-]_t = 4[CCl_4]_0[1 - \exp(-kt)]. \quad [4]$$

Rearranging and taking the natural log of both sides yields

$$\ln\{1 - [Cl^-]_t/(4[CCl_4]_0\} = -kt. \quad [5]$$

A plot of the left side of Eq. [5] vs. time yields a straight line with a slope of –k, the apparent rate constant.

In our work, we determine $[CCl_4]_0$ by the difference between the final $[Cl^-]$ with complete hydrolysis [i.e., data from long-term hydrolysis at 100°C (PNNL) or 130°C (SUNY-Cortland)] and the initial $[Cl^-]$ [data

7

from time=0 samples]. We then calculate the value of the left side of Eq. [5] for each time data point in the given experiment. Regression of these values against the corresponding incubation times yields the slope, from which the apparent rate constant (k_{app}) is obtained by multiplying by -1. For reaction vessels with headspace, partition equilibrium is assumed and the apparent rate constant is corrected to obtain a rate constant normalized to zero headspace (k_{zhs}) by

$$k_{zhs} = k_{app} [1 + (K_H')(V_v/V_l)] \qquad [6]$$

where K_H' is the dimensionless Henry's Law vapor-partition coefficient and V_l and V_v are the equilibrium liquid and vapor volumes (see Section 2.4 below).

The half-life in years of the hydrolysis of CT for a given temperature is calculated from the rate constant k_{zhs} by

$$t_{1/2} = (3.168e\text{-}8)*\ln(2)/k_{zhs} \qquad [7]$$

where the first factor on the right side converts the rate constant from seconds to years.

Activation energies are calculated from values of k_{zhs} at several temperatures using the logarithmic form of the Arrhenius expression

$$\ln(k_{zhs}) = \ln(A) - (E_a/R)(1/T) \qquad [9]$$

where A is the preexponential factor (s^{-1}), Ea is the activation energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the reaction temperature (K). Regression of $\ln(k_{zhs})$ vs. (1/T) yields a slope of E_a/R, from which E_a is readily calculated.

2.4   Determination of Liquid-Vapor Partition Coefficients

An apparatus was designed and fabricated, and techniques were developed to measure liquid-vapor partition coefficients at the temperatures of our experiments, as the only available data (Gossett, 1987) did not extend beyond 35°C. The apparatus (Figure 4 bottom), which consists of a 50-mL round-bottom Pyrex® bulb with the neck replaced by a 5-cm length of 1-mm ID capillary glass flared at the top and fitted with a 0.25-in fitting (Swagelok®) so that a rubber septum directly sealed to the glass, is similar to the ZHR but with no second fill-tube. The bulb can be rinsed, filled, and drained using a syringe. In practice, the bulb is weighed empty, filled using a 50-mL syringe and long wide-bore needle, weighed full and sampled with a 1-mL syringe and 17-gauge needle, then drained about one-third using the 50-mL syringe, quickly sealed, reweighed, and immersed in the thermostat bath. The bulb is shaken several times over a 15 – 30 minute interval, then sampled through the septum while still in the bath to determine an equilibrium solution concentration. During the draining process, some solution is deposited in the capillary to serve as an indicator that no solution or vapor escapes through the septum. The initial and equilibrium samples are then hydrolyzed to completion as with the ZHR experiments. The dimensionless partition coefficient turns out to be simply calculated as

$$K_{lv} = [(C_0 - C_f)/C_f](V_l/V_v) \qquad [7]$$

where C_0 and C_f are the initial and equilibrium liquid concentrations of Cl^- in ppm, and V_l and V_v are the equilibrium liquid and vapor volumes.

3.0   Hydrolysis Rates for Carbon Tetrachloride

A total of five hydrolysis experiments are underway at PNNL, of which two are for hydrolysis in DI H_2O, two in Hanford groundwater, and one in a suspension of Hanford-Site sediment in Hanford groundwater. Table 1 shows the status of the experiments with respect to sampling as of 30 September 2008. Experiments at 40°C and higher have been fully sampled and analyzed. Hydrolysis rates are quite slow at temperatures below 40°C, and several years may be required for the experiment at 20°C.

Table 1. Status of PNNL carbon tetrachloride (CT) hydrolysis experiments.					
	Deionized H_2O, 11 ppm CT	Deionized H_2O, 162 ppm CT	Hanford Groundwater, 31 ppm CT	Hanford Groundwater, 359 ppm CT	Hanford Sediment in Groundwater, 263 ppm CT
Temperature, °C	--------------Fraction of experiment sampled as of 30 September 2008--------------				
20	70	70	60	60	60
30	90	90	100	80	80
40	100	100	100	100	100
50	100	100	100	100	100
60	100	100	100	100	--
70	100	100	100	100	--

At SUNY-Cortland, more than 35 kinetics experiments have been completed, including data at temperatures up to 93°C for correlation with the previous data reported by Jeffers et al. (1996). Only data from the most reliable of these experiments are reported here.

3.1   Deionized Water

Most of the new data available at the writing of this report are for hydrolysis in DI H_2O at temperatures from 40° to 93°C. These are summarized in Table 2. For the PNNL data, both k_{app} and k_{ZHS} [normalized using K_H' values from Gossett (1987)] are reported. We note that the data of Gossett (1987) were collected at temperatures of 10-35°C. We used the parameters fitted by Gossett to extrapolate his results to the higher temperatures in our study. Although we have conducted experiments to measure K_H' values at relevant temperatures, the results of these have been inconclusive (see Section 4). As a consequence all rate constant values must be considered provisional pending further review of the data.

Table 2. Provisional rate constants for hydrolysis of carbon tetrachloride in deionized H_2O.

Temperature, °C	Initial CCl_4 Concentration, mg L^{-1}	k_{zhs} SUNY, s^{-1}	k_{zhs} PNNL, s^{-1}	k_{app} PNNL, s^{-1}	K_H' (Gossett, 1987)
93.0	340	3.50e-6	--	--	--
88.0	163	1.98e-6	--	--	--
80.5	62	8.50e-7	--	--	--
70.0	369	2.32e-7	--	--	--
70.0	323	2.33e-7	--	--	--
70.0	163	--	3.12e-7	7.22e-8	7.432
70.0	11	--	3.43e-7	7.91e-8	7.432
60.0	323	5.63e-8	--	--	--
60.0	162	--	7.18e-8	2.16e-8	5.205
60.0	11	--	6.99e-8	2.10e-8	5.205
50.0	323	1.40e-8	--	--	--
50.0	301	1.34e-8	--	--	--
50.0	162	--	1.41e-8	5.44e-9	3.562
50.0	11	--	1.53e-8	5.91e-9	3.562
40.0	314	2.18e-9	--	--	--
40.0	162	--	2.87e-9	1.39e-9	2.377
40.0	11	--	1.67e-9	8.10e-10	2.377
30.0	290	3.59e-10	--	--	--
30.0	321	4.00e-10	--	--	--
30.0	162	--	5.53e-10	3.27e-10	1.543
25.0	460	1.62e-10	--	--	--
20.0	162	--	1.25e-10	8.74e-11	0.971

The earlier high-temperature data published by Jeffers et al. (1996) were not corrected for headspace, as this was assumed to have negligible effect in his minimum headspace bulbs. Recent measurements of the headspace in similar bulbs suggest that a headspace:liquid ratio of 0.02 would make a reasonable estimate for the earlier work. To help compare the values obtained in the current project with those from the earlier work we have calculated k_{zhs} values for the Jeffers et al. (1996) data by the same approach used for the PNNL data. These are summarized in Table 3.

To visualize the current data in comparison to the earlier high-temperature data of Jeffers et al. (1996) all the k_{zhs} values are shown in an Arrhenius plot along with the k_{app} values for the high-temperature data (Figure 5). From this plot it is immediately apparent that the high-temperature data on the upper left side of the plot are significantly affected by the headspace correction even

Table 3. Rate constants for hydrolysis of carbon tetrachloride in deionized H_2O at high temperatures as reported by Jeffers et al. (1996) (k_{app}) and as corrected for an assumed 2% headspace:liquid ratio using extrapolated values of K_H' from Gossett (1987) (k_{zhs}).

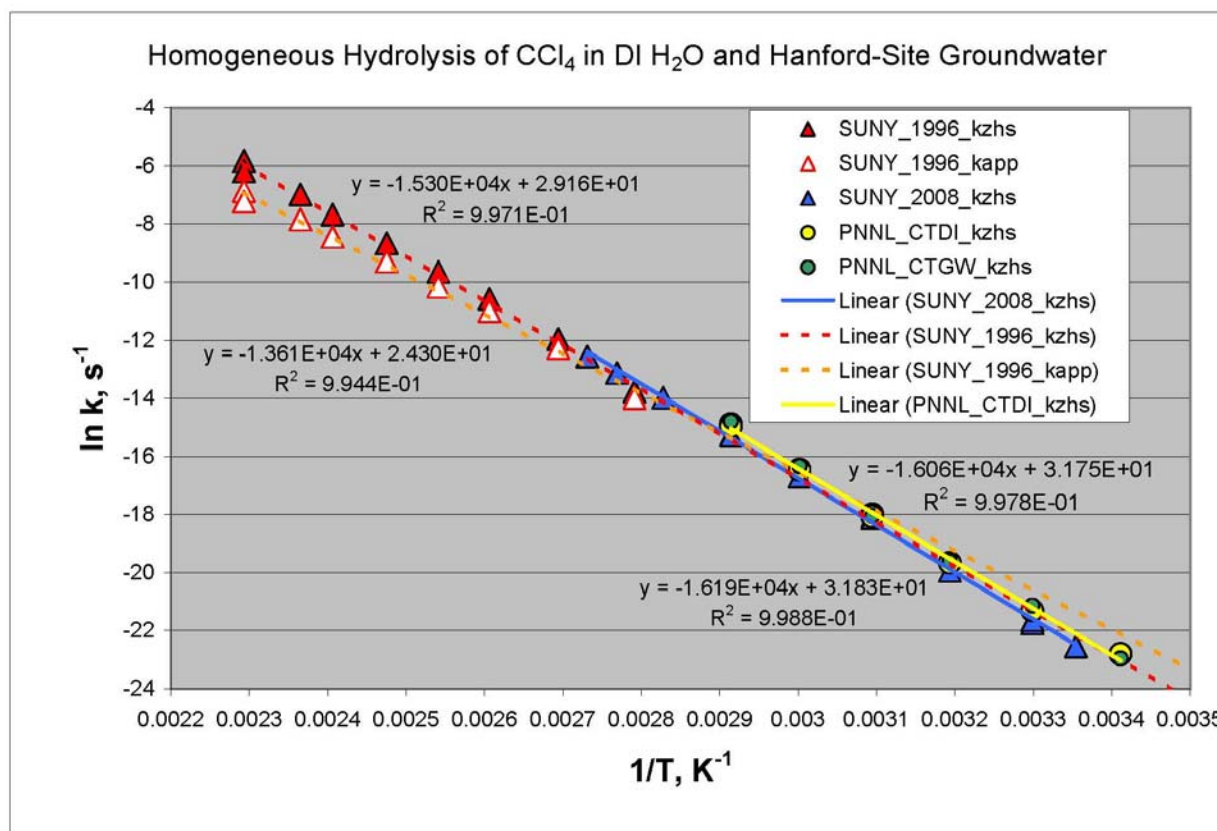| Temperature, °C	Nominal Initial CCl_4 Concentration, mg L^{-1}	k_{zhs}, s^{-1}	k_{app}, s^{-1}	K_H' (Gossett, 1987)
163.0	40	2.94e-3	1.04e-3	90.634
163.0	40	2.05e-3	7.29e-4	90.634
149.7	40	9.25e-4	3.92e-4	67.973
142.5	40	4.34e-4	2.15e-4	57.711
130.9	40	1.73e-4	9.19e-5	43.789
120.4	40	6.44e-5	3.85e-5	33.601
110.6	40	2.55e-5	1.68e-5	25.870
98.0	40	6.36e-6	4.67e-6	18.140
85.0	40	1.04e-6	8.36e-7	12.199

Figure 5. Arrhenius plot of k_{zhs} data generated in this study (through 2008) along with k_{app} data as reported by Jeffers et al. (1996) and the 1996 data normalized to k_{zhs} assuming a 2% headspace:liquid ratio and the extrapolated Henry's Law coefficients of Gossett (1987).

with only 2% headspace. When these data are extrapolated to lower temperatures (dashed lines), better agreement with the 2008 data is obtained for the headspace-corrected 1996 data than for the original k_{app} data reported by Jeffers et al. (1996).

On the lower right side of the plot, the PNNL data are slightly, but consistently, higher than those from the SUNY ZHR approach. The consistent Arrhenius slopes obtained for the PNNL and SUNY ZHR datasets, however, suggest that the differences in rates are due to a systematic error in one or the other approach. Although there is uncertainty in the values of the extrapolated partition coefficient used (K_H') to estimate k_{zhs} for the PNNL data, this uncertainty would disproportionally affect the higher temperature data and lead to different Arrhenius slopes for the two approaches. One such factor that could cause such a shift would be the accuracy of the determination of total CCl_4 concentration in the two approaches. If the PNNL approach consistently underestimated this parameter or if the SUNY approach consistently overestimated this parameter, then the PNNL data would consistently yield higher rate constants than the SUNY data. An interlaboratory cross-comparison study would help answer this question.

Overall, the measured 2008 rate constants are slower than those that would have been predicted by extrapolation of the 1996 k_{app} data to lower temperature (i.e., the dashed orange line in Fig. 5). For example, the Arrhenius equation,

$$k = Ae^{(-Ea/RT)} \qquad [8]$$

where A is the pre-exponential factor (s^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant (8.314 J mol^{-1} K^{-1}), and T is the temperature (K), predicts from the 1996 k_{app} data a rate of 4.77e-9 s^{-1} at 40°C, whereas the SUNY k_{zhs} value measured is 2.18e-9 s^{-1}, a factor of 2.2 slower. The gap between predicted and measured values increases to a factor of 3 at groundwater temperatures judging from the current trends in the data.

Values for E_a and A determined from the regression lines in the Arrhenius plot (Figure 5) are summarized in Table 4. A single value for a k_{zhs} dataset consisting of the normalized Jeffers et al. (1996), SUNY 2008 and PNNL 2008 datasets is also reported. These data show reasonable agreement in E_a among the three separate k_{zhs} datasets, and a substantial increase in E_a and A over the values reported by Jeffers et al. (1996) for the k_{app} dataset. The value of E_a for the combined k_{zhs} dataset is slightly lower than any of the separate datasets due to the generally higher rate constants obtained in the PNNL 2008 experiments. This may be an artifact of the use of the extrapolated Henry's Law coefficients of Gossett (1987) as discussed in Section 4. Resolution of this potential artifact is needed before the values from the combined dataset can be used with confidence.

Also shown in Table 4 are the corresponding half-lives at 16°C calculated using the Arrhenius parameters to estimate the rate constants and then inserting them into

$$t_{1/2} = \ln(2)/k. \qquad [9]$$

These clearly show the 2- to 3-fold differences between the original extrapolated data and those estimated from the current results. To reiterate, however, the current results are considered provisional pending collection of data at lower temperatures and resolution of the gas-liquid partitioning behavior in the PNNL experiments.

Table 4. Provisional Arrhenius parameters for hydrolysis of carbon tetrachloride in deionized H_2O and corresponding provisional half-lives estimated for 16°C.

Dataset	E_a, kJ mol^{-1}	A, s^{-1}	$t_{1/2}$ (16°C), yr
Jeffers et al. (1996), k_{app}	113	3.6e10	170
Jeffers et al. (1996), k_{zhs}	127	4.6e12	450
SUNY 2008, k_{zhs}	135	6.7e13	680
PNNL 2008, k_{zhs}	134	6.1e13	470
All, k_{zhs}	128	5.8e12	410

For comparison to previous published analyses that have represented rate constants as half-life values, we converted the rate constants shown in Table 2 to equivalent half-life values using Eq. [9] and listed them in Table 5.

Table 5. Provisional half-life values for hydrolysis of carbon tetrachloride in deionized H_2O based on rate constants listed in Table 2.

Temperature, °C	Initial CCl$_4$ Concentration, mg L^{-1}	$t_{1/2}$ using k_{zhs} SUNY, yr	$t_{1/2}$ using k_{zhs} PNNL, yr	$t_{1/2}$ using k_{app} PNNL, yr	K_H' (Gossett, 1987)
93.0	340	0.0063	--	--	--
88.0	163	0.011	--	--	--
80.5	62	0.026	--	--	--
70.0	369	0.095	--	--	--
70.0	323	0.094	--	--	--
70.0	163	--	0.070	0.30	7.432
70.0	11	--	0.064	0.28	7.432
60.0	323	0.39	--	--	--
60.0	162	--	0.31	1.0	5.205
60.0	11	--	0.31	1.0	5.205
50.0	323	1.6	--	--	--
50.0	301	1.6	--	--	--
50.0	162	--	1.6	4.0	3.562
50.0	11	--	1.4	3.7	3.562
40.0	314	10.	--	--	--
40.0	162	--	7.7	16.	2.377
40.0	11	--	13.	27	2.377
30.0	290	61.	--	--	--
30.0	321	55.	--	--	--
30.0	162	--	40.	67.	1.543
25.0	460	140.	--	--	--
20.0	162	--	180.	250.	0.971

3.2 Groundwater and Sediment

The hydrolysis data for Hanford groundwater are summarized in Tables 6 (rate constants) and 7 (half-lives). Analogous data for a suspension of Hanford-Site sediment in Hanford groundwater are given in Tables 8 and 9. An Arrhenius plot of these data with those data collected for deionized water systems is shown in Figure 6. As before, all data are provisional pending further evaluation and additional data.

Table 6. Provisional rate constants for hydrolysis of carbon tetrachloride in Hanford groundwater.

Temperature, °C	Initial CCl$_4$ Concentration, mg L^{-1}	k_{zhs} SUNY, s^{-1}	k_{zhs} PNNL, s^{-1}	k_{app} PNNL, s^{-1}	K_H' (Gossett, 1987)
70	306	--	3.75e-7	8.55e-8	7.432
70	24	--	4.41e-7	9.97e-8	7.432
60	402	4.67e-8	--	--	--
60	306	--	8.03e-8	2.38e-8	5.205
60	24	--	1.14e-7	2.57e-8	5.205
50	306	--	1.45e-8	5.51e-9	3.562
50	24		2.86e-8	6.46e-9	3.562
48.6	464	1.38e-8	--	--	--
40	306	--	3.04e-9	1.46e-9	2.377
30	306	--	6.58e-10	3.86e-10	1.543

Table 7. Provisional half-life values for hydrolysis of carbon tetrachloride in Hanford-Site groundwater based on rate constants listed in Table 6.

Temperature, °C	Initial CCl$_4$ Concentration, mg L^{-1}	$t_{1/2}$ using k_{zhs} SUNY, yr	$t_{1/2}$ using k_{zhs} PNNL, yr	$t_{1/2}$ using k_{app} PNNL, yr	K_H' (Gossett, 1987)
70	306		0.059	0.26	7.432
70	24		0.050	0.22	7.432
60	402	0.47			--
60	306		0.27	0.92	5.205
60	24		0.19	0.86	5.205
50	306		1.5	4.0	3.562
50	24		0.77	3.4	3.562
48.6	464	1.6			--
40	306		7.2	15.	2.377
30	306		33.	57.	1.543

The key observation is that the presence of Hanford-Site sediment seems to increase the rate of CT hydrolysis relative to that in homogeneous solution and this effect becomes more pronounced as temperature decreases. Essentially no effect of sediment is seen at temperatures of 40°C and higher, but a significant (p <0.05) effect is seen at 30°C. The data available at 20°C, while currently at the limits of detectability, suggest an even greater relative impact of sediment than at 30°C. These results are consistent with the hypothesis that sorption of CT to sediment surfaces lowers the effective activation energy of the hydrolysis reaction thereby increasing the rate of

Table 8. Provisional rate constants for hydrolysis of carbon tetrachloride in suspensions of Hanford-Site sediment in Hanford groundwater.

Temperature, °C	Initial CCl_4 Concentration, mg L^{-1}	k_{zhs} PNNL, s^{-1}	k_{app} PNNL, s^{-1}	K_H' (Gossett, 1987)
50	244	1.65e-8	6.65e-9	3.562
40	244	3.26e-9	1.64e-9	2.377
30	244	9.57e-10	5.84e-10	1.543
20	244	3.10e-10	2.21e-10	0.971

Table 9. Provisional half-life values for hydrolysis of carbon tetrachloride in suspensions of Hanford-Site sediment in Hanford-Site groundwater based on rate constants listed in Table 7.

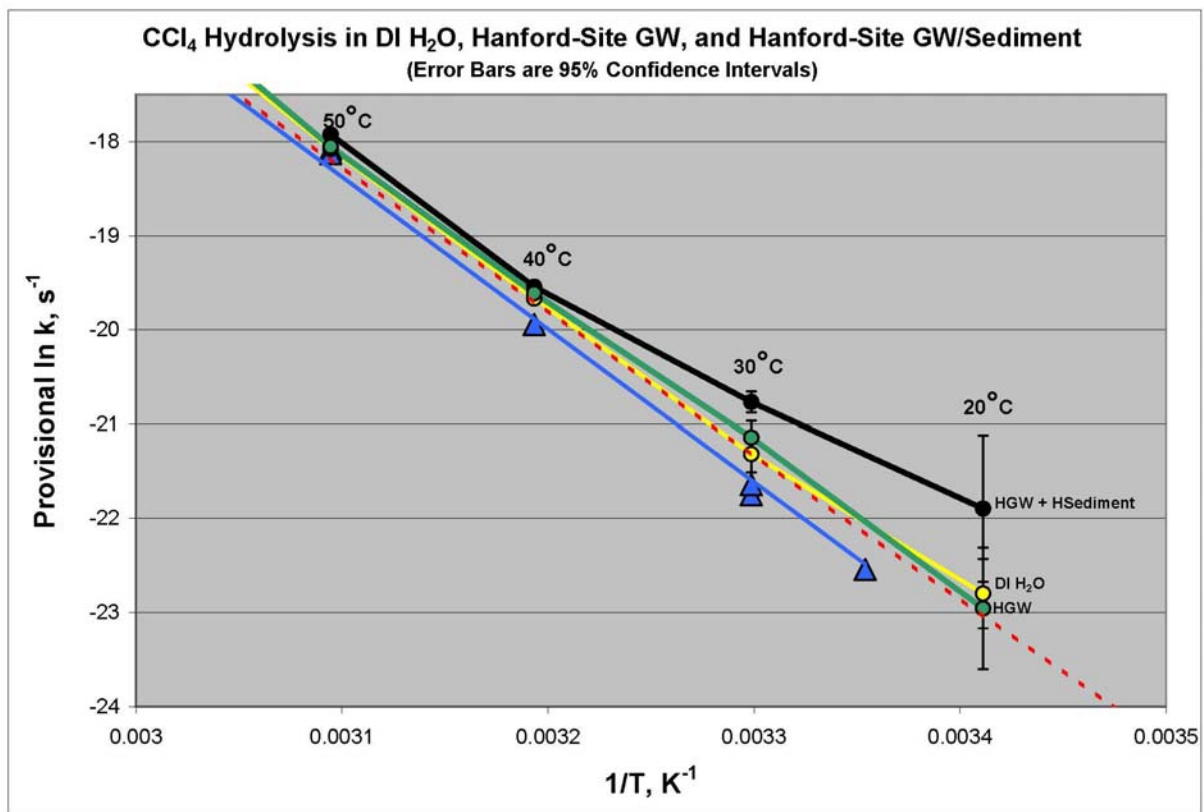| Temperature, °C	Initial CCl_4 Concentration, mg L^{-1}	$t_{1/2}$ using k_{zhs} PNNL, yr	$t_{1/2}$ using k_{app} PNNL, yr	K_H' (Gossett, 1987)
50	244	1.3	3.3	3.562
40	244	6.7	13.	2.377
30	244	23.	38.	1.543
20	244	71.	99.	0.971

Figure 6. Arrhenius plot of k_{zhs} data for hydrolysis of carbon tetrachloride in deionized H_2O, Hanford groundwater, and suspensions of oxidized Hanford sediment in Hanford groundwater. Blue triangles are SUNY data for deionized H_2O using ZHRs.

hydrolysis. The fraction of the total CT present in the system that is sorbed to the solid phase would be expected to increase as temperature decreases, consistent with the observed data.

Another possible explanation of these results is that biotic activity, which would likely be optimized at temperatures close to the ambient groundwater temperature to which the microorganisms are acclimated, could have caused enhanced degradation of CT by processes other than hydrolysis. However, biotic activity would be expected to yield some CF as a product (Bouwer and McCarty, 1983; Criddle et al., 1990b; Laine and Cheng, 2007) except in pure cultures under denitrifying conditions (Criddle et al., 1990a; Phanikumar et al., 2002; Tatara et al., 1993). To assess whether biotic activity was responsible for the results with sediment, we tested 16 samples from the hydrolysis treatments involving deionized H_2O, Hanford-Site groundwater, and the treatment with Hanford-Site sediment for evidence of CF formation during the experiment. Chloroform hydrolyzes at a slower rate than CT at the near-neutral pHs of the experiment, and so a very slight increase in the CF to CT ratio (i.e., CF/CT) would be expected in samples where hydrolysis occurred relative to those where it did not (i.e., samples quenched at 4ºC). On the other hand, if biotic activity were responsible for CT degradation, a large increase in CF/CT would be expected from generation of CF as product of the biotic degradation reaction. In general, the results of these analyses showed no significant difference in CF/CT between samples that showed loss of CT (presumably from hydrolysis) and those showing no loss. There were two exceptions, both for 40ºC samples (one in Hanford-Site groundwater and the other involving Hanford-Site sediment) that may have been contaminated during preparation. We conclude therefore that the observed enhancement of observed hydrolysis rates due to the presence of sediment does not stem from biotic activity.

To give a rough idea of the magnitude of the sediment effect on the CT hydrolysis rate at 16°C (i.e., ambient groundwater temperature), we fit a quadratic equation to the sediment hydrolysis data and extrapolated down to 16°C. The rate constant calculated from this extrapolation was $2.8e\text{-}10 \text{ s}^{-1}$, which corresponds to a half-life of 78 years. This compares very favorably with the estimated half-life of 470 years obtained from the parallel PNNL study in the absence of sediment (Table 4) and suggests a 6-fold increase in CT hydrolysis rate may occur due to the sorption to the sediment. Clearly, continued data collection at 30° and 20°C will be helpful in further refining the estimated significance of this effect.

4.0   Liquid-Vapor Partition Coefficients

As discussed in Section 3, rate constants derived from ZHR experiments at SUNY-Cortland were slightly, but consistently, lower than the k_{zhr} values from sealed vial experiments performed at PNNL. The PNNL calculations used Henry's Law constants (K_H') for CCl_4 derived from a temperature fit of experimental values (Gossett, 1987) but extrapolated considerably beyond the temperature range of his experiments to correct the apparent rate constant to values of k_{zhs}. Recognizing that Henry's Law is strictly valid only at infinite dilution, direct measurements of liquid-vapor partition coefficients (K_{lv}) at the concentrations used in our experiments were conducted at SUNY-Cortland in an attempt to provide experimental values valid at the temperatures of our joint experiments.

The results of these measurements are shown in Figure 7, along with the data (measured and extrapolated) of Gossett (1987) and back-calculated values from the PNNL hydrolysis determinations in deionized water. These back-calculations were done by assuming that the k_{zhs} value obtained at SUNY-Cortland was correct, and the value of K_H' used in the PNNL data calculations was varied until the PNNL k_{zhs} value matched that of SUNY-Cortland.

Clearly, the K_{lv} results obtained by SUNY and Gossett (1987) differ substantially, with good agreement obtained only at near ambient temperatures. Further, the precision of the two datasets differed substantially. The SUNY method yielded values with relative standard deviations (RSDs) of about 15%
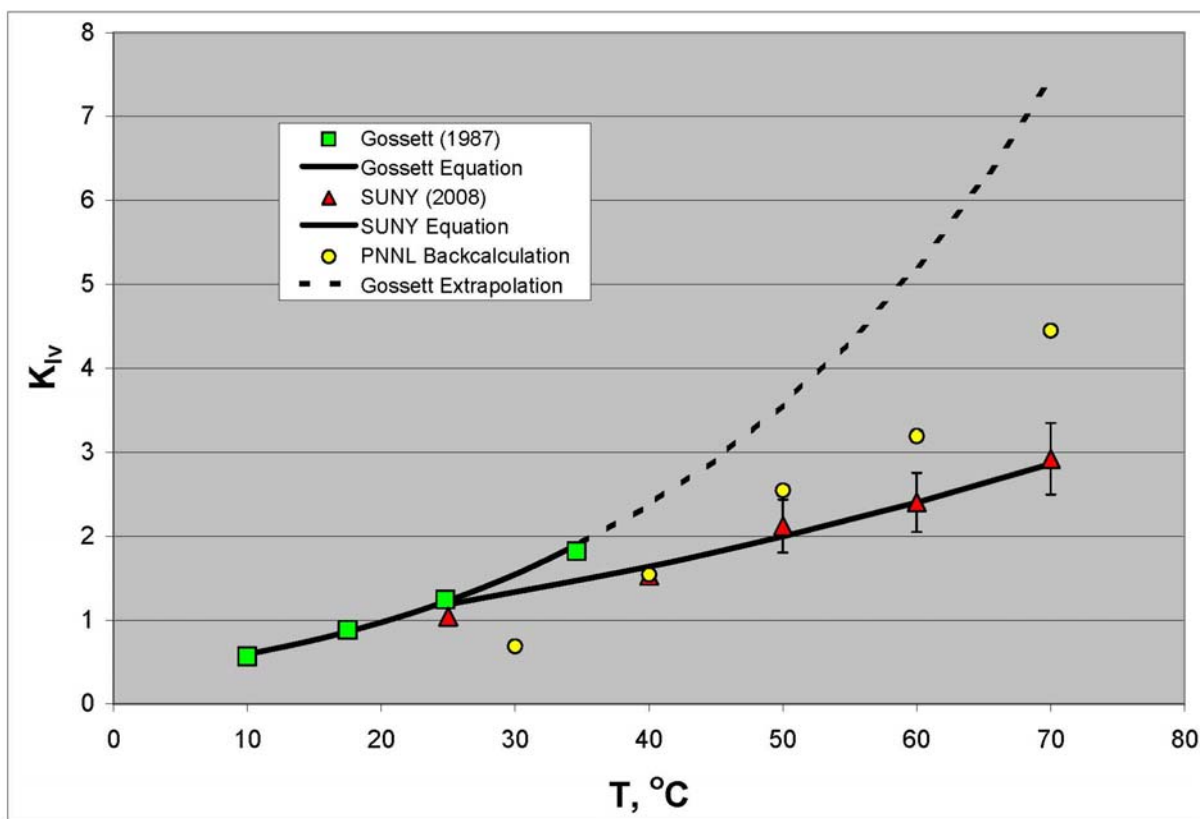

Figure 7. Values of K_H' determined and extrapolated to higher temperatures from Gossett (1987) together with direct determinations of K_{lv} at SUNY-Cortland and back-calculated values of K_{lv} derived from PNNL hydrolysis-rate determinations in deionized H_2O.

(only one experiment was performed each at temperatures of 25 and 40°C, so no RSDs are calculated for those two data points), whereas Gossett (1987) reported RSDs of 3-4%. Gossett measured headspace concentrations of CT and used a valved syringe to avoid errors due to pressure differences between the vials being sampled and the ambient laboratory atmosphere. Because SUNY samples collected were liquids, such precautions were not deemed necessary. Gossett (1987) equilibrated his samples for at least 18 hours, if not longer, whereas the equilibration time used in the SUNY determinations was 15-30 minutes. No data were collected during the SUNY experiments to verify that equilibrium was attained between the liquid and gaseous phases. Just as importantly, the back-calculated values of K_{lv} needed to obtain agreement between the PNNL and SUNY k_{zhr} values do not match well at all with the SUNY determined values of K_{lv}. The sum of these factors leads us to question whether the SUNY experiments were successful in measuring true values of K_{lv}. We reluctantly conclude therefore, that the best values available are still those of Gossett (1987) extrapolated to higher temperatures as necessary.

5.0   General Observations and Future Work

In general, the data obtained in this study agree well with those from higher temperatures, once the effects of partitioning into the vapor phase are taken into account. The net result is that slower rates of hydrolysis of CT *in homogeneous solution* are being measured at near-ambient temperatures than would have been predicted before this study. The precise size of the difference at ambient groundwater temperatures awaits further data. An estimate based on the current data yields homogeneous hydrolysis rates that are two to three times slower at groundwater temperatures than would be predicted from the open literature.

This bleak result is more than offset, however, by the demonstration of a catalytic enhancement of the hydrolysis rate stemming from sorption of CT to Hanford-Site sediment. Based on extrapolation from the current data available, we estimate that a six-fold enhancement of hydrolysis rate (relative to that in homogeneous solutions) is likely at a groundwater temperature of 16ºC. This estimated increase in rate translates into a 78-year half-life for CT dissolved in Hanford-Site groundwater that is in contact with Hanford-Site sediment. Based on analysis of the products, we are confident that the effect of the sediment is not due to biotic or to other redox-related degradation processes. Further, we see no difference in rates obtained in deionized water or in Hanford-Site groundwater, only an effect of Hanford sediment.

We must emphasize that the hydrolysis rate data at 20ºC, in contrast to those at higher temperatures, are preliminary and have low statistical power. While significant ($p < 0.05$) differences between the heterogeneous and homogeneous systems are seen at 30ºC, the results at 20ºC are not statistically significant at this level due to limited data and the very slow nature of the reaction. More time is needed to collect data at these low temperatures to improve the statistical power of our observation.

Given the critical need for hydrolysis rate data at temperatures relevant to groundwater systems, we have three recommendations for future work. First, we recommend a continuation of the sampling and analysis of the remaining long-term sealed-ampule experiments described in this report. As indicated in Table 1, these are primarily 20ºC and 30ºC experiments. The data at 20°C, which are most germane to the groundwater environment, will likely take two more years before they are complete. Second, due to the importance of heterogeneous effects, we recommend the continuation of sampling and analysis for a similar set of experiments looking at hydrolysis rates of CT and CF in contact with individual minerals (montmorillonite, kaolinite, albite, and muscovite) or Hanford-Site sediment, and, for CF, in homogeneous solutions. These experiments were set up under a separate project funded by a congressional earmark (EM-22) for which funding expired at the end of FY08. Third, we strongly recommend development of a $^{13}C/^{12}C$ isotope ratio mass spectrometry (IRMS) approach for determination of hydrolysis rates at groundwater temperatures and relevant CT and CF concentrations. The technique is sensitive enough that we expect to be able to shorten the time required for a rate-constant determination by 20-fold. Thus, a 5-year experiment conducted by the sealed-ampule approach could be shortened to 3 months by the IRMS approach. This sensitivity also would allow the IRMS technique to be used to follow hydrolysis rates at concentrations found in groundwater plumes at Hanford.

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