

Carbon Tetrachloride and Chloroform Attenuation Parameter Studies: Heterogeneous Hydrolytic Reactions Progress in FY2007

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1.0 Introduction

1.1 Rationale

Between 1955 and 1973, an estimated 750,000 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. Of this amount, some CT reached the groundwater more than 70 m below the ground surface and formed a plume of 10 km² extent. Recent information has shown 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.

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 CT/CF 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 in this project 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 CT/CF plume at Hanford. Previous field and modeling efforts have focused on determining the impacts of other attenuation mechanisms including dispersion and dilution processes and CT sorption to Hanford sediments (Riley et al. 2005). The abiotic degradation processes, however, are not well understood.

Previous determinations of the hydrolysis rate for CT 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 FY 2006 the Hanford Groundwater Project initiated a study to determine the homogeneous hydrolysis rate of CT at

temperatures closer to ambient groundwater temperatures. The homogeneous hydrolysis study will also provide initial observations of possible sediment effects on the CT 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 CT homogeneous hydrolysis study may be important in quantifying the overall attenuation capacity for the CT/CF plume. First, the study is not investigating the hydrolysis rate for CF, a prominent co-contaminant with CT. Under homogeneous conditions, CF degrades by both neutral and base-catalyzed hydrolysis. As with CT, 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 CT but with comparable uncertainty. Again, as with CT, the overall abiotic degradation rate of CF at ambient temperatures may be a combination of homogeneous and heterogeneous hydrolysis reactions as well as other redox-related heterogeneous reactions. Second, the CT 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 CT or CF hydrolysis in the Hanford subsurface. Unfortunately, the already sparse literature on the hydrolysis of CT and CF is completely silent on the question of heterogeneous effects for these two compounds.

The present project is designed to complement and leverage the work recently initiated in the CT homogeneous hydrolysis project. We are addressing the uncertainty in the homogeneous hydrolysis rate for CF using an approach similar to that in the CT homogeneous hydrolysis project. We are also conducting thorough investigations of the possible impacts of mineral surfaces on the hydrolysis rates of both CT and CF. 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 FY07. 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 two-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 CT and CF at the Hanford Site

1.2 Project Objectives

The major objectives of this project are to

- 1) Determine the neutral and base-catalyzed homogeneous hydrolysis rates for CF under near-ambient temperatures.
- 2) Determine the impact and mechanisms of representative Hanford mineral surfaces on the hydrolysis of CT at near-ambient temperatures.
- 3) Determine the impact and mechanisms of representative Hanford mineral surfaces on the neutral and base-catalyzed hydrolysis of CF at near-ambient temperatures.

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 sediment or mineral phases in groundwater using ampoules 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 ampoules (headspace:liquid ratio of about 1:50) and a home-built zero-headspace reactor. Work at SUNY-Cortland also includes direct determinations of aqueous:vapor partition coefficients for CT and CF using a home-built reactor.

2.0 Technical Approach and Method Development

Technical work is organized under three major tasks: Task 1 focuses on the neutral and base-catalyzed homogeneous rates of CF; Task 2 focuses on the heterogeneous rate of CT; and Task 3 focuses on the neutral and base-catalyzed heterogeneous rates of CF. 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 follow.

2.1 Task Descriptions and Experimental Design

2.1.1 Task 1—Neutral and Base-Catalyzed Homogeneous Hydrolysis of CF

The overall experimental design involves collection of data at six temperatures covering the range of 20°-70°C. Samples are incubated in sterile deionized (DI) water adjusted to one of three initial pHs (3, 8, or 12) with H₂SO₄ or a 0.1 M sodium phosphate buffer, at one concentration (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, with an additional two replicates reserved for verification of reaction mechanism and 14 vials reserved for determination of initial and total concentrations. Thus, the total number of experimental units is $6 \times 3 \times 1 \times (7 \times 10 + 14) = 1512$.

2.1.2 Task 2—Heterogeneous Hydrolysis of CT

The experimental approach for determination of heterogeneous hydrolysis of CT differs in some respects from that of Task 1 because of logistical constraints. Data are collected at four temperatures (20°, 30°, 40°, and 50°C) and at one concentration (400 ppm). Samples are incubated in one of four environments consisting of sterile Hanford groundwater alone or in the presence of fine-grained mineral powder. As in Task 1, we conduct five replicate analyses for each treatment combination at each of ten times during the experiment, with an additional two replicates reserved for verification of reaction mechanism and 14 vials reserved for determination of initial and total concentrations. Thus, the total number of experimental units is $4 \times 1 \times 4 \times (7 \times 10 + 14) = 1344$.

2.1.3 Task 3—Neutral and Base-Catalyzed Heterogeneous Hydrolysis of CF

The experimental approach for heterogeneous hydrolysis of CF closely follows that of Task 2 with the exception that experiments with Hanford groundwater and sediment suspended in groundwater are included with the four mineral experiments. The total number of experimental units is $4 \times 1 \times 6 \times (7 \times 10 + 14) = 2016$.

2.2 Groundwater, Sediment, and Minerals

Uncontaminated Hanford groundwater was obtained from Well 699-49-100C located near the Yakima barricade west and up-gradient 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. Although not measured specifically for the samples in this project (aside from chloride) the composition of the water from this well is summarized from Hanford Environmental Information System (HEIS) data in Table 1.

Constituent/Property	Value ($\mu\text{g L}^{-1}$ unless otherwise indicated)
SO ₄ ²⁻	75000
NO ₃ ⁻	13000
Cl ⁻	19000
F ⁻	300
Ca ²⁺	60000
Mg ²⁺	21000
Na ⁺	25000
K ⁺	7500
Fe (valence unspecified)	30
Alkalinity	175000
Total Organic Carbon	1000
Electrical Conductivity ($\mu\text{S cm}^{-1}$)	570
pH (log units)	7.75

Uncontaminated Hanford sediment 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.

The mineralogy of the Hanford sediment was determined by X-ray diffraction of the whole sediment and of the clay (<2- μm particle size) fraction according to the procedures of Amonette (1994a, 1994b). As discussed in section 3.2.1, the results of this analysis were used to select four minerals for use in mono-mineralic heterogeneous hydrolysis experiments.

2.3 Laboratory Procedures

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 H₂O 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.

For CF, 0.5 liter of PRA-grade CF (>99.9% pure, Sigma-Aldrich, 324019) is purified to remove the amylene stabilizer by contact with 80 g of 13X molecular sieve followed by vacuum degassing. This purified reagent CF is then used to prepare a saturated stock solution by adding at least 100 ml to about 2 L of deionized H₂O or Hanford groundwater in a volumetric flask that is capped and allowed to shake as for the CT solution for at least two weeks at room temperature. The nominal concentration of CF in the saturated stock solution is 8000 mg L⁻¹.

Starting solutions for hydrolysis determinations are prepared in 1.2-L PTFE gas sampling bags (Alltech 41004, Deerfield, IL). The appropriate masses of CT/CF 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. For CF experiments, pH control is provided by addition of H₂SO₄ (pH 3) or a 0.1 M sodium phosphate buffer (pH 8 or 12). Also, 10 µL of neat perchloroethene (PCE), which has an hydrolysis half-life of 10⁹ years (Jeffers et al. 1989), is added to serve as an internal standard during gas chromatographic (GC) analyses. Some water is added and headspace in the bag eliminated before the CT/CF stock solution, pH reagent, and PCE are added. A typical final volume in the bag is 800 mL and initial CT/CF 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 a dispenser designed for organic liquids (Dispensette® Organic, BrandTech Scientific, Essex, CT) and the contents dispensed through a large-bore stainless-steel needle into ampoules for immediate sealing.

The hydrolysis experiments are conducted in 1-mL (nominal volume) glass ampoules (Figure 2 left, Wheaton 176772, Millville, NJ). These ampoules typically have an internal volume of 2.4 ml when sealed. We add 1.6 ml of aqueous sample to the ampule, leaving 0.8 ml as headspace. The ampoules are sealed within 15 s of sample addition using an automatic ampule sealer (Figure 2 right, Ampulmatic Model 290 001, Bioscience, Inc., Bethlehem, PA).

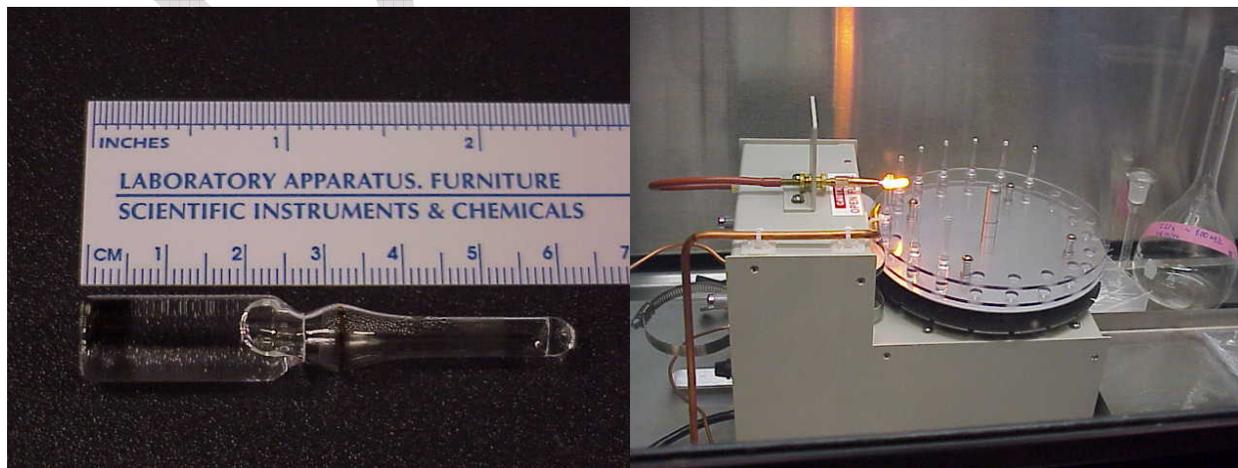


Figure 2. Ampule (left) and automatic ampule sealer (right) used for PNNL hydrolysis experiments.

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 CT/CF in the ampules. The other seven are stored at 4°C where hydrolysis rates are negligible (except for CF at pH 12, see below). 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

$$V_{HS} = (m_{tot}^A - m_{tot}^B + m_{Amp+CT/CF})/\rho_{H_2O} - (m_{Amp}/\rho_{Amp}) - (m_{CT/CFsoln}/\rho_{CT/CFsoln}) \quad [1]$$

where m_{tot}^A = mass of syringe filled with H₂O, m_{tot}^B = mass of syringe filled with sealed ampule and H₂O, $m_{Amp+CT/CF}$ = mass of filled ampule, ρ_{H_2O} = density of water, m_{Amp} = mass of empty ampule, ρ_{Amp} = density of glass in ampule, $m_{CT/CFsoln}$ = mass of solution in ampule, and $\rho_{CT/CFsoln}$ = 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 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. For CT and all CF samples except those at pH 12, quenching is achieved by storage in a 4°C refrigerator. When convenient for analysis (or immediately for pH-12 CF samples), 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 H₂O for several days with two changes of H₂O during the first day, and one change on each subsequent day. The transferred samples remain at 4°C until IC analysis. For all CF samples, 0.5 mL of hexane is added to the vial to extract CF from the aqueous solution. This is necessary to prevent damage



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

to the IC column. 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 of CT 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 $20^\circ\text{-}70^\circ\text{C}$ 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 constructed this year, 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.



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.

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 a 10-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 $\frac{1}{4}$ inch Swagelok® fitting and affords a glass to 10-mm GC-septum 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 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.

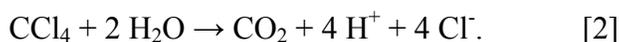
The ZHR and all associated glassware, syringes, and needles are heat sterilized before use. The deionized water is boiled and sparged with a flow of He to remove dissolved air. This prevents the formation of air bubbles inside the reactor to which reactant could partition during a run and is an important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

The Cortland experiments with CF utilized 0.01 M NaOH solutions. Concentrations of CF were about 50 – 150 mg L⁻¹, or 0.00126 – 0.00378 M, low enough that the base concentration changed little during the experiment (<10% completion) and pseudo-first-order kinetics could be assumed. An advantage of the dilute base approach is that the OH⁻ concentration can be measured directly and there is no temperature dependence on any acid/base equilibrium constant, as would be the case with any buffer solution. Another advantage is that kinetics properly uses concentration rather than activity which is the quantity reported by a pH meter. The concentration can be measured directly and accurately by titration of a primary standard, potassium hydrogen phthalate, in this case. Lastly, at this base concentration, CF hydrolyzes to completion in two days at 70°C, so to determine final concentration the entire ZHR could be placed in an oven, stopcock open until the temperature had equilibrated, affording the entire reactor contents for final analysis.

2.4 Calculations

2.4.1 Carbon Tetrachloride. The hydrolysis of CT follows the overall reaction



The rate law for this reaction is

$$-\text{d}[\text{CCl}_4]/\text{dt} = (1/4)\text{d}[\text{Cl}^-]/\text{dt} = k[\text{CCl}_4] \quad [3]$$

which, upon integration yields

$$[\text{Cl}^-]_t = 4[\text{CCl}_4]_0[1 - \exp(-kt)]. \quad [4]$$

Rearranging and taking the natural log of both sides yields

$$\ln\{1 - [\text{Cl}^-]_t/(4[\text{CCl}_4]_0)\} = -kt. \quad [5]$$

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 $[\text{CCl}_4]_0$ by the difference between the final $[\text{Cl}^-]$ with complete hydrolysis [i.e., data from long-term hydrolysis at 100°C (PNNL) or 130°C (SUNY-Cortland)] and the initial $[\text{Cl}^-]$ [data 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

$$k_{\text{zhs}} = k_{\text{app}} [1 + (K_{\text{H}}')(V_{\text{v}}/V_{\text{l}})] \quad [6]$$

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 2.3 below).

2.4.2 Chloroform. The hydrolysis of CF follows two parallel pathways. One of these is independent of pH, whereas the other is first order in OH^- . The rate of CF hydrolysis, therefore, is the sum of the rates of the two pathways:

$$-d[\text{CHCl}_3]/dt = (k_{\text{N}} + k_{\text{B}}[\text{OH}^-])[\text{CHCl}_3] \quad [7]$$

where k_{N} is the rate constant for the neutral (pH-independent) pathway, and k_{B} is the rate constant for the base-catalyzed pathway.

The neutral hydrolysis pathway is

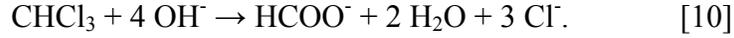


and the corresponding integrated and rearranged rate law is analogous to that for CT shown in Eqs. [3]-[5]:

$$\ln\{1 - [\text{Cl}^-]_t/(3[\text{CHCl}_3]_0)\} = -k_{\text{N}}t. \quad [9]$$

Neutral hydrolysis is the dominant pathway at $\text{pH} < 4$ and Eq. [9] can be used to estimate CF hydrolysis under those conditions.

At pH > 4, the base-catalyzed hydrolysis pathway becomes important (and is dominant at pH > 8) due to the strong nucleophilic character of the hydroxyl ion. The overall reaction can be written as



The rate law for the base-catalyzed hydrolysis reaction is second-order overall, being first order in both CHCl₃ and OH⁻:

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_B[\text{CHCl}_3][\text{OH}^-] \quad [11]$$

When the concentrations of CHCl₃ and OH⁻ differ by a factor of ten or more, the reactant at higher concentration remains essentially constant during the first stages of the reaction and the reaction becomes pseudo-first-order (PFO). Thus, at pH 12 and higher, where OH⁻ is in excess, the PFO rate law becomes

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_{\text{Bpfo1}}[\text{CHCl}_3] \quad [12]$$

where $k_{\text{Bpfo1}}/[\text{OH}^-]_0 = k_B$. By analogy to Eqs. [4] and [5], the rearranged integrated rate law then becomes

$$\ln\{1 - [\text{Cl}^-]_t/(3[\text{CHCl}_3]_0)\} = -k_B t \quad [13]$$

At pH 8, where CHCl₃ is in excess and the base-catalyzed rate is still much faster than the neutral rate, the PFO rate law becomes

$$-d[\text{CHCl}_3]/dt = -(1/4)d[\text{OH}^-]/dt = (1/3)d[\text{Cl}^-]/dt = k_{\text{Bpfo2}}[\text{OH}^-] \quad [14]$$

where $k_{\text{Bpfo2}}/[\text{CHCl}_3]_0 = k_B$, and by analogy to Eqs. [12] and [13],

$$\ln\{1 - [\text{Cl}^-]_t/(3[\text{OH}^-]_0)\} = -k_B t \quad [15]$$

At pH > 8, then Eqs. [13] or [15] can be used to estimate overall CF hydrolysis given the dominance of k_B . Between pH 4 and pH 8, neither hydrolysis mechanism (i.e., neutral or base-catalyzed) is dominant and the overall hydrolysis rate for chloroform is best approximated using both rate constants as in Eq. [7].

2.4.3 Half-life. Half-lives can be calculated when first-order kinetics apply. They can also be calculated for second-order kinetic systems, if these are converted to pseudo-first-order and with the caveat that the concentration of the “constant” reactant indeed remains constant for the duration of the reaction. Thus, for CT, and for CF at pH < 4 or > 8, the half-life is estimated by

$$t_{1/2} = (3.168e-8)\ln(2)/k \quad [16]$$

where the first factor on the right side converts the rate constant from seconds to years, and k can be k_{zhs} , k_N , or k_B . For CF between pH 4 and pH 8, the half life can be estimated by substituting $k_N + k_B[\text{OH}^-]$ for k in Eq. [16].

2.4.4 Activation Energy. Activation energies are calculated from values of k at several temperatures using the logarithmic form of the Arrhenius expression

$$\ln(k) = \ln(A) - (E_a/R)(1/T) \quad [17]$$

where k can be k_{zhs} , k_N , or k_B (s^{-1}), A is the pre-exponential factor (s^{-1}), E_a is the activation energy (J mol^{-1}), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), and T is the reaction temperature (K). Regression of $\ln(k)$ vs. $(1/T)$ yields a slope of E_a/R , from which E_a is readily calculated. As with half-lives, the use of pseudo-first-order rate constants (such as k_B) carries the assumption that the “constant” reactant remains constant and the values of A and E_a thus calculated are only valid for the specific concentration of “constant” reactant.

2.5 Determination of Liquid-Vapor Partition Coefficients

At SUNY-Cortland, 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 for CT (Gossett, 1987) did not extend beyond 35°C . The apparatus (Figure 4 bottom) comprised a 50-mL Pyrex® bulb with a 10-cm long 2-mm id capillary tube, much like the ZHR but with no second fill-tube. The bulb is weighed empty, filled using the 50-mL syringe and long wide-bore needle, weighed full and sampled with the 1-mL syringe and 17-gauge needle, then drained about one-third using the 50-mL syringe, quickly sealed and immersed in the thermostat bath. The bulb is shaken several times over a 15 – 20 minute interval, then sampled through the septum to determine an equilibrium solution concentration. 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

$$K_{lv} = [(C_0 - C_f)/C_f](V_l/V_v) \quad [22]$$

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

3.0 Hydrolysis Rate Experiments

3.1 Homogeneous Chloroform Experiments

A total of four homogeneous hydrolysis experiments with CF have been started at PNNL, two at pH 3, one at pH 8, and one at pH 12. Hydrolysis is rapid at pH 12 and those experiments are complete (Table 2). In addition, the highest-temperature (60°C and 70°C) experiments at pH 8 are also complete or nearly so (Table 2). The hydrolysis rates are considerably slower at pH 8 and temperatures below 60°C , and several years may be required to obtain useful data at 20°C .

Several years will also be required to obtain hydrolysis rates at pH 3, where only neutral hydrolysis is important.

	pH 3, 33 ppm CF, 1 mM H ₂ SO ₄	pH 3, 229 ppm CF, 1 mM H ₂ SO ₄	pH 8, 182 ppm CF, 0.1 M phosphate	pH 12, 285 ppm CF, 0.1 M phosphate
Temperature, °C	----- fraction of experiment sampled as of September 2007 -----			
70	50	50	100	--
60	30	30	90	--
50	10	10	30	100
40	10	10	10	100
30	--	10	10	100
20	--	10	10	100

At SUNY-Cortland, seven experiments at six temperatures between 22°C and 60°C and pH 12 have been completed.

As noted in Table 2, only base-catalyzed experiments conducted at pH 8 and 12 are at a stage where rate constants can be calculated. These data are summarized in Table 3 along with the initial reactant concentrations and the dimensionless Henry's Law constants derived from Gorgenyi et al. (2002). Note that all the PNNL data were collected in 0.1 m phosphate buffers, and that the PNNL data at 70°C and 60°C were collected at pH 8. All rate constant values must be considered provisional pending further review of the data.

Temperature, °C	Initial CHCl ₃ Concentration, mg kg ⁻¹	Initial OH ⁻ Concentration, mol kg ⁻¹	k _B , SUNY, kg mol ⁻¹ s ⁻¹	k _B , PNNL (0.1 m phosphate), kg mol ⁻¹ s ⁻¹	K _H ' (Gorgenyi et al., 2002)
70	182	1.72e-6	--	3.22e-1	0.663
60	182	1.72e-6	--	5.64e-2	0.541
60	58	9.74e-3	8.70e-3	--	--
55	157	9.59e-3	4.55e-3	--	--
50	285	2.44e-2	--	4.19e-3	0.417
40	157	9.59e-3	5.18e-4	--	--
40	58	9.74e-3	5.18e-4	--	--
40	285	2.44e-2	--	6.46e-4	0.296
30.15	50	1.01e-2	1.22e-4	--	--
30	190	9.74e-3	1.00e-4	--	--
30	285	2.44e-2	--	1.05e-4	0.209
22	157	9.59e-3	2.98e-5	--	--
20	285	2.44e-2	--	1.57e-5	0.137

To help visualize the results, an Arrhenius plot of the base-catalyzed rate data is shown in Fig. 5. From this plot and Table 3 it is clear that the PNNL and SUNY data collected at pH 12 are in

good agreement, although the slopes (activation energies) differ by about 20%. The PNNL rate constants from pH 8 data, however, are quite a bit higher than one would expect from the pH 12 data.

The two primary differences between the PNNL and SUNY experimental approaches are the presence of headspace in the ampoules and the use of phosphate buffer in the PNNL experiments. The headspace would influence the results only if the Henry's law constants were very large and in doubt. This does not seem to be the case, and so we think it likely that the differences are due to the use of a phosphate buffer. Hydrogen phosphate (HPO_4^{2-}) ions, like hydroxyl ions, are strong nucleophiles and can initiate hydrolysis-like reactions that would release Cl^- ions to solution (Schwarzenbach et al., 1993, p. 359-365; Swain and Scott, 1953). Differences in the speciation of phosphate with pH (predominantly PO_4^{3-} at pH 12 and a mixture of HPO_4^{2-} and H_2PO_4^- at pH 8) could account for the difference in values of k_B between the data collected at these two pHs. Apparently the protonated phosphate ions are much stronger nucleophiles than the PO_4^{3-} ion. Bicarbonate ions (HCO_3^-) are roughly equivalent to HPO_4^{2-} in terms of their nucleophilicity, and their presence in most groundwaters suggest that substantial enhancement (as much as a doubling) of CF hydrolysis occurs in slightly alkaline to alkaline systems.

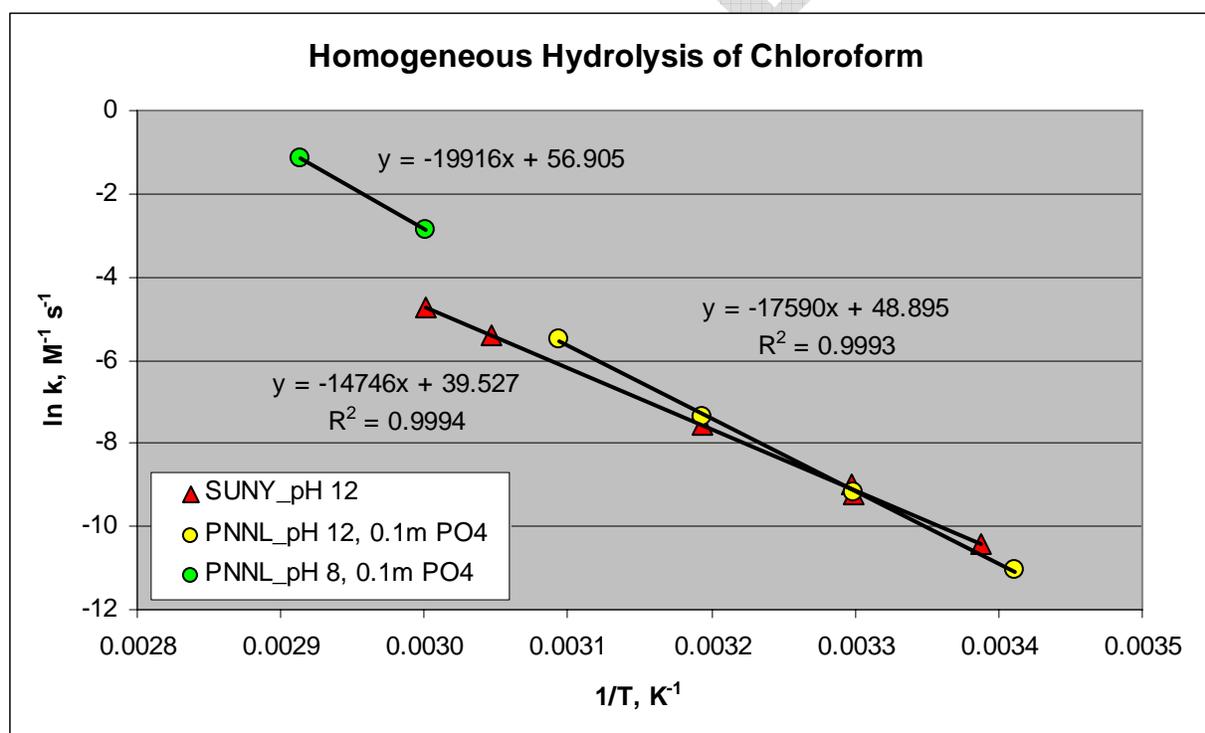


Figure 5. Arrhenius plot of homogeneous hydrolysis data for CF at pH 12 and pH 8.

The activation energies for base-catalyzed CF hydrolysis are 123 kJ mol^{-1} for the SUNY experiments at pH 12, 146 kJ mol^{-1} for PNNL experiments in 0.1 m phosphate at pH 12, and about 165 kJ mol^{-1} for PNNL experiments in 0.1 m phosphate at pH 8. These compare with a value of 105 kJ mol^{-1} reported from high-temperature experiments by Jeffers et al. (1989) using minimal headspace (ca. 2%) ampoules without correction for Henry's law.

3.2 Heterogeneous Experiments

3.2.1 Sediment characterization and selection of minerals. The results of the textural and mineralogical analysis of the Hanford sediment are summarized in Table 4. Based on the particle-size analysis, the sediment can be classified as a silt loam. Quartz was the most abundant mineral, followed by smectite and plagioclase feldspar (60% anorthite/40% albite). Other layer silicates, such as mica/illite and kaolin/serpentine were present in measurable quantities.

Based on this analysis and the ready availability of mineralogically pure samples, we selected montmorillonite (a type of smectite), kaolinite, albite, and muscovite (a type of mica) as the four minerals for testing of heterogeneous effects on hydrolysis. Quartz, although the most abundant mineral, was not selected because of its ubiquity in soils and sediments. Any heterogeneous effect seen in our tests with bulk sediment that exceeded that for the minerals selected for testing could be attributed to quartz or to a highly reactive mineral that could not be detected by our method. One such class of reactive minerals would be the iron and manganese oxides. If much higher reactivity is seen with the bulk sediment than with our mineralogically pure samples, further work could involve these more reactive but less abundant minerals. We were careful to select minerals that had no Fe(II) in their structures, and ensured this by oxidatively sterilizing them with 10% hydrogen peroxide to convert labile Fe(II) to Fe(III).

Particle Size Class	----- weight percent -----
Sand (>53 μm)	0
Silt (2-53 μm)	78
Clay (<2 μm)	22
Bulk Mineralogy	
Quartz	49
Plagioclase (60:40 An:Al)	10
Potassium feldspar	1
Smectite	30
Mica/illite	6
Kaolin/serpentine	5

3.2.2 Experiment status.. The status of the experiments with CF is summarized in Table 5, and with CT in Table 6. A total of seven heterogeneous hydrolysis experiments (out of nine planned) were started in FY2007, with the remaining two scheduled for early in FY2008. All the experiments involve suspensions of minerals or Hanford sediment in Hanford groundwater. Insufficient data have been collected to calculate provisional rate constants for any of these experiments.

Table 5. Status of PNNL heterogeneous CF hydrolysis experiments in Hanford groundwater.					
	Hanford Sediment	Montmorillonite	Kaolinite	Albite	Muscovite
Temperature, °C	----- fraction of experiment sampled as of September 2007 -----				

50	50	10	10	10	Start October 2007
40	30	10	10	10	Start October 2007
30	20	10	10	10	Start October 2007
20	20	10	10	10	Start October 2007

Table 6. Status of PNNL heterogeneous CT hydrolysis experiments in Hanford groundwater.				
	Montmorillonite	Kaolinite	Albite	Muscovite
Temperature, °C	----- fraction of experiment sampled as of September 2007 -----			
50	20	10	10	Start October 2007
40	10	10	10	Start October 2007
30	10	10	10	Start October 2007
20	10	10	10	Start October 2007

4.0 General Comments and Future Work

The main achievements in FY2007 were 1) initiation of eleven major experiments at PNNL involving a total of nearly 4000 ampules and preparation for an additional two experiments, 2) completion of one major set of experiments at pH 12 for base-catalyzed hydrolysis of CF involving work at both PNNL and SUNY, 3) collection of preliminary evidence suggesting that nucleophiles other than OH⁻ (such as HPO₄²⁻ and HCO₃⁻) could also accelerate the abiotic degradation of CF, and 4) development of techniques at SUNY-Cortland for zero-headspace hydrolysis experiments and for determination of liquid-vapor partition coefficients at elevated temperatures.

In FY2008, we plan to initiate the last two heterogeneous hydrolysis experiments with muscovite as the mineral, continue sampling/analyzing these and the other eleven experiments, conduct parallel experiments with smectite and kaolinite at SUNY-Cortland, and verify the liquid-vapor partition coefficients for CT and CF.

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