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# Abiotic and biotic transformation of 1,1,1-trichloroethane under methanogenic conditions

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## **RATE OF ABIOTIC FORMATION OF 1,1-DICHLOROETHYLENE FROM 1,1,1-TRICHLOROETHANE IN GROUNDWATER**

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### **ABSTRACT**

Vogel, T.M. and McCarty, P.L. 1987. Rate of abiotic formation of 1,1-dichloroethylene from 1,1,1-trichloroethane in groundwater. *J. Contam. Hydrol.*, 1: 299–308.

The abiotic transformation of the halogenated aliphatic compound, 1,1,1-trichloroethane (TCA), to 1,1-dichloroethylene (1,1-DCE) in groundwater was measured in the laboratory at 20°C and neutral pH. The measured pseudo first-order disappearance rate constant for TCA was  $0.11 \pm 0.16 \text{ yr}^{-1}$  (95% confidence interval). The formation rate constant for 1,1-DCE could be determined with greater precision, and was found to be  $0.040 \pm 0.003 \text{ yr}^{-1}$ . These results indicate the 95% confidence interval for TCA half-life at 20°C and pH 7 in homogeneous solution is 2.8 to 19 yrs. While these results confirm that 1,1-DCE is a product from the abiotic transformation of TCA, other products such as acetic acid are also possible, although they were not measured.

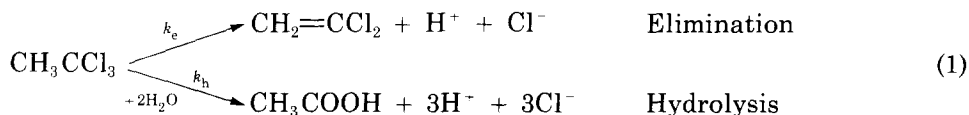
### **INTRODUCTION**

The solvent 1,1,1-trichloroethane (TCA) is one of the most common contaminants in groundwaters used as a source of drinking water supply in the United States (Westrick et al., 1984). Since groundwater moves slowly and residence times are in the order of years to centuries, the eventual fate of TCA in groundwater is of environmental interest. Under reducing environmental conditions, TCA can be biologically converted by reductive dehalogenation (Bouwer and McCarty, 1983; Gossett, 1985; Parsons and Lage, 1985), with 1,1-dichloroethane (1,1-DCA) being formed as an intermediate product (Gossett, 1985; Parsons and Lage, 1985).

The abiotic transformation of TCA in water has also been reported. Several abiotic studies carried out at elevated temperatures (from 55° to 160°C under pressure) indicated TCA was transformed to acetic acid (Britton and Reed, 1932; Walraevens et al., 1974; Mabey et al., 1983). Rates of abiotic TCA transformation at lower temperatures were estimated by extrapolation. Such extrapolation has resulted in suggested half-lives for TCA at neutral pH and 25, 20, and 10°C of 0.6, 1.4, and 7 yrs, respectively (Mabey et al., 1983). Two studies were carried out at temperatures more characteristic of groundwaters. Dilling et al. (1975) reported a TCA half-life of 0.5 yrs at 25°C in deionized water, but transformation products were not measured. Pearson and McConnell (1975)

reported a TCA half-life of 0.8 yrs at 10°C and pH 8 in seawater, and indicated 1,1-DCE was the major product.

Thus, the current information indicates abiotic TCA transformation results in two possible products, one from elimination and the other from hydrolysis:



where

$$k = k_e + k_h \quad (2)$$

In this example, the overall rate constant  $k$  is assumed to equal the sum of the hydrolysis rate constant ( $k_h$ ) and the elimination rate constant ( $k_e$ ).

In the long-term laboratory study reported here, the rate of abiotic transformation of low concentrations of TCA added to groundwater was measured in the laboratory at 20°C and neutral pH, conditions that more resemble an actual contaminated groundwater environment.

#### MATERIALS AND METHODS

Two studies were conducted. In the first, groundwater was obtained from a freshwater aquifer in San Jose, California, by pumping from an extraction well. The water was supplemented with TCA, and its fate under both biotic and abiotic conditions was monitored over several months. In the second study, a more defined media (BOD dilution water) was used to evaluate the biotic and abiotic fate of TCA over several months in order to obtain additional information to confirm or refute the results of the first study.

In the first study, the groundwater was divided into three fractions, each of which was supplemented with about 1800 µg/L TCA. The first fraction was used without further addition. The second was supplemented with about 10 mg/L each of acetone and 2-propanol, solvents that are sometimes found as groundwater contaminants and can serve as substrates for bacterial growth. The third fraction was also supplemented with acetone and 2-propanol, but in addition, 10 mg/L HgCl<sub>2</sub> was added to serve as a biological inhibitor.

Each of the above fractions was added to a series of 240-mL bottles, which were then capped without headspace using teflon-coated seals. The bottles were kept at 20°C in the dark, and a set was periodically sacrificed over a 198-day period of analysis for acetone, 2-propanol, a range of halogenated volatile organics, and on occasion, pH and dissolved oxygen (DO).

The organic analyses were conducted by a certified commercial laboratory (Stoner Laboratories, Santa Clara, California). Two gas chromatographic (GC) procedures were used for the chlorinated compounds: (1) purge-and-trap using a Hall electrolytic conductivity detector (HECD) and a 240 cm × 2 mm Carboxpack B/1% SP-1000 column; (2) liquid-liquid extraction using pre-tested

iso-octane and an electron capture detector (ECD) with a 240 cm  $\times$  2 mm Carbopack B/1% SP-1000 column as well as a 180 cm  $\times$  2 mm n-octane/Porasil C column. Acetone and 2-propanol were determined by distilling sample portions using a Barrett distilling receiver (Corning 3622). Distillate, collected in the receiving tube surrounded by cold packs, was examined by GC using a 240 cm  $\times$  2 mm Carbopack B/3% SP-1500 column and a flame ionization detector. The reported limit of detection for acetone and 2-propanol was 20  $\mu$ g/L.

In the second study, 60 ml serum bottles were filled with BOD dilution water containing dissolved oxygen and bacterial seed (APHA, 1980) to which about 130  $\mu$ g/L of TCA (Baker Analytical, Baker Chem. Co.) was added. Mercuric chloride (10 mg/L) was added to some samples to serve as abiotic controls. The samples were stored in the dark at 20°C for up to 380 days. In this study, analyses were conducted at the Stanford University Water Quality Control Research Laboratory, using three different methods for confirmation of products. First, a modified liquid-liquid extraction procedure (after Henderson et al., 1976) was used. Using glass syringes (Hamilton) and 20 G needles, iso-octane (1.0 mL) was added to a serum bottle with simultaneous removal of water. After adding an internal standard (bromochloropropane), the bottles were vigorously mixed for 30 min on a shaker table, 5  $\mu$ L of the iso-octane was injected into a Grob injector and onto a 200 cm  $\times$  2.5 mm 10% squalane Chromosorb W/AW column in an isothermal (50°C) GC (Tracor) with an ECD. The second method involved use of a 5-mL sample with a purge-and-trap system (Tekmar) connected to a GC with column similar to the above followed by a HECD with Coulson modification. The third method involved closed-loop stripping followed by GC/mass spectrometry (Finnigan 4000 with Incos data system) as described by [Graydon et al. \(1983\)](#). This procedure was used to confirm transformation product identification.

TABLE 1

pH, and dissolved oxygen (DO) in TCA-amended groundwater samples (20°C)

Day of Study	Control		Acetone/2-propanol		Acetone/2-propanol HgCl <sub>2</sub>	
	DO	pH	DO	pH	DO	pH
	(mg/L)		(mg/L)		(mg/L)	
0	8.0		5.8	7.6	3.7	7.5
9	7.9	7.4		7.4		6.6
16	7.0	7.5	< 0.1	7.4	5.1	6.5
23	6.4	7.5	< 0.1	7.4	1.8	6.5
30	7.1	7.4	< 0.1	7.3	1.5	6.5
38	2.7	7.3	< 0.1	7.2	3.4	6.6
44	7.0	7.4	< 0.1	7.3	6.2	6.6
51	5.7	7.4	< 0.1	7.3	3.5	6.7

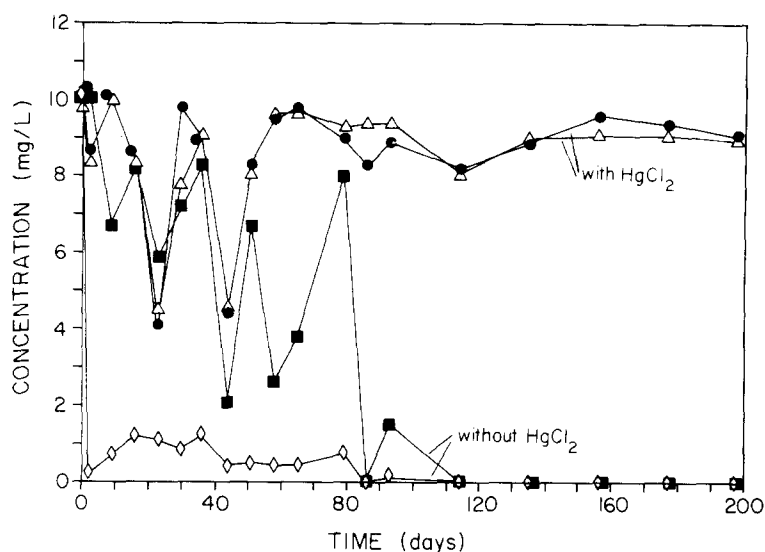


Fig. 1. Acetone (filled symbols) and 2-propanol (unfilled symbols) concentrations versus time for groundwater fractions; acetone and 2-propanol without  $\text{HgCl}_2$  (■, ◇) and acetone/2-propanol with  $\text{HgCl}_2$  (●, △).

## RESULTS

Measurements of dissolved oxygen (DO) and pH during the first 51 days of the first study are given in Table 1. The initial DO concentration was lower in the samples with acetone and 2-propanol, probably resulting from organic biological oxidation during the few hours before measurement and  $\text{HgCl}_2$  addition. Measureable DO concentrations remained in the first and third fractions, but decreased to zero in the biologically active second fraction supplemented with acetone and 2-propanol. The 2-propanol was removed rapidly in this second fraction, and acetone disappeared after about three months

TABLE 2

Summary of statistical analysis for TCA pseudo first-order decay rate constant ( $k$ ) in groundwater samples ( $20^\circ\text{C}$ )

Fraction	Number of data $n$	TCA zero-time intercept ( $\mu\text{g/L}$ ) <sup>a</sup>	TCA average conc. ( $\mu\text{g/L}$ ) <sup>b</sup>	$k$ ( $\text{yr}^{-1}$ ) <sup>a</sup>
Control	19	$1800 \pm 140$	$1810 \pm 140$	$-0.026 \pm 0.25$
Acetone/isopropanol	19	$1470 \pm 100$	$1450 \pm 170$	$0.097 \pm 0.27$
Acetone/isopropanol/ $\text{HgCl}_2$	19	$1410 \pm 130$	$1350 \pm 130$	$0.26 \pm 0.36$
All data (normalized)	57			$0.11 \pm 0.16$

<sup>a</sup>  $\pm$  values represent 95% confidence intervals.

<sup>b</sup>  $\pm$  values represent one standard deviation.

(Fig. 1). Since acetone and IPA were not consumed in fraction 3 (Fig. 1) and DO remained in these samples, inhibition of biological activity by the added  $\text{HgCl}_2$  is indicated.

TCA concentration as a function of time in the three fractions is shown in Fig. 2. The initial TCA concentrations, based upon the zero-time intercepts and 95% confidence intervals from a least-squares regression analysis of  $\log_e$  of concentrations (Table 2), indicates TCA concentration in the first fraction was significantly higher than in the other two. The difference probably resulted from losses during the initial preparation of the samples for storage.

Assuming that TCA transformation can be modeled as a first-order reaction, the following equations were applied:

$$C/C_0 = e^{-kt} \quad (3)$$

$$t_{1/2} = 0.69/k \quad (4)$$

where  $C$  = concentration of TCA at time  $t$ ;  $C_0$  = initial TCA concentration;  $k$  = pseudo first-order rate constant, and  $t_{1/2}$  is the half life for TCA. The negative slope of the regression lines for  $\log_e$  of TCA concentration versus time would give the pseudo first-order decomposition rate constants. The calculated rate constants together with 95% confidence intervals are listed in Table 2. The calculated decay rates for TCA are not significantly different than zero for any of the samples. When data from the three fractions are normalized by division of concentration by the initial concentrations listed in Table 2 for the respective samples, the three data sets were found not to be significantly different from one another. These normalized data were then pooled to obtain better precision on the decay rate constant and its 95% confidence interval, resulting

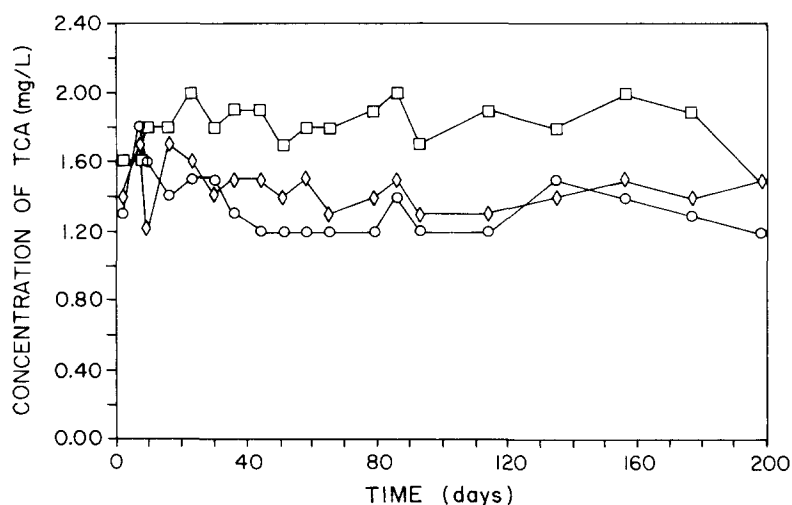


Fig. 2. TCA concentration versus time for three groundwater fractions; water only ( $\square$ ), water plus acetone and 2-propanol ( $\diamond$ ), and water plus acetone and 2-propanol with  $\text{HgCl}_2$  ( $\circ$ ).

TABLE 3

Concentrations of volatile organic compounds (except TCA and 1,1-DCE) measured in ground-water samples (20°C) over period of first study ( $\mu\text{g/L}$ )<sup>a</sup>

	No. of analyses	Control	Acetone/ 2-propanol	Acetone/ 2-propanol/ $\text{HgCl}_2$
Freon	19	$3.2 \pm 0.4$	$2.9 \pm 0.3$	$2.8 \pm 0.5$
Trichloroethylene	19	< 0.5	< 0.5	< 0.5
Tetrachloroethylene	19	$7.5 \pm 0.4$	$6.5 \pm 0.5$	$6.0 \pm 0.6$
Xylene + Ethylbenzene	19	< 5	< 5	$21 \pm 5$
1,1-DCA <sup>b</sup>	8	$11 \pm 1$	$11 \pm 2$	$8 \pm 1$

<sup>a</sup>  $\pm$  values represent standard deviation.

<sup>b</sup> Data were not obtained over first 120 days of study.

in values also listed in Table 2. The upper boundary for the decay rate constant using the 95% confidence interval can be obtained from the pooled data with a single-tailed analysis, yielding a value of  $0.25 \text{ yr}^{-1}$ , corresponding to a minimum half-life for abiotic transformation of TCA under the experimental conditions used here of 2.8 yrs. The actual half-life is likely to be longer.

Volatile organic compounds other than TCA and 1,1-DCE were found present in the original samples because the groundwater used was contaminated (Table 3). However, the only compound for which concentration change was statistically significant during the course of the study was 1,1-DCE (Fig. 3). TCA was the only chlorinated compound present in sufficiently high con-

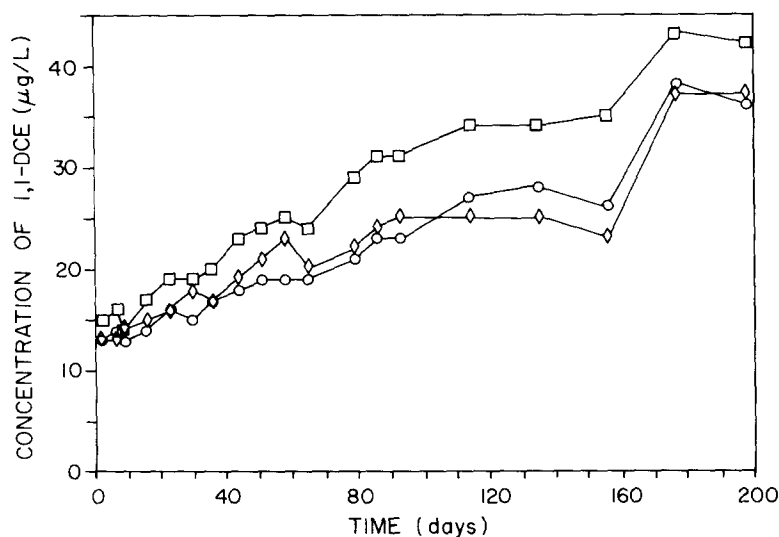


Fig. 3. 1,1-DCE concentration versus time for three groundwater fractions; water only (□), water plus acetone and 2-propanol (◇), and water plus acetone and 2-propanol with  $\text{HgCl}_2$  (○).

centration from which the increase in 1,1-DCE concentration could have resulted. Thus, 1,1-DCE was assumed to be formed from abiotic dehydrohalogenation of TCA as reported by Pearson and McConnell (1975). The rate constant of TCA transformation to 1,1-DCE is given by  $k_e$ , which is assumed equivalent to the 1,1-DCE formation rate constant:

$$\frac{d[1,1\text{-DCE}]}{dt} = k_e[\text{TCA}] \quad (5)$$

Because the TCA concentration decreased very little (about 6%) during the study period, the following equation was found appropriate for data analysis:

$$\frac{[1,1\text{-DCE}]_t - [1,1\text{-DCE}]_0}{[\text{TCA}]} = k_e t \quad (6)$$

In order to determine  $k_e$ , the initial concentration of 1,1-DCE,  $[1,1\text{-DCE}]_0$ , in each sample was needed. This was obtained by a least-squares extrapolation of the data to time equals zero (Table 4). The data sets were each normalized by subtracting the initial 1,1-DCE values from the measured 1,1-DCE concentrations  $[1,1\text{-DCE}]_t$ , and dividing by the average 1,1-TCA concentration,  $[\overline{\text{TCA}}]$  (Table 2). A least-squares regression analysis of the left-hand side of eqn. (6) versus  $t$  was made for each data set in order to determine  $k_e$  (Table 4). The  $k_e$  values differed from an average value by less than 10% for samples with or without an active bacterial population, dissolved oxygen, or  $\text{HgCl}_2$ , and thus the transformation of TCA to 1,1-DCE appears to be abiotic. Since the results for the sets did not differ significantly from one another, the normalized data were pooled to determine  $k_e$  with greater precision, resulting in a value of  $0.040 \pm 0.003 \text{ yr}^{-1}$  (Table 4).

In order to confirm the finding that 1,1-DCE was formed from dehydrochlorination of TCA, the second study was conducted using TCA-supplemented BOD dilution water at pH 7 and incubated at 20°C. No 1,1-DCE was detectable initially in these samples. After 380 days of incubation, 4 samples of dilution

TABLE 4

Summary of statistical analysis for 1,1-DCE first-order formation rate constant ( $k_e$ )<sup>a</sup> in groundwater samples (20°C)

Sample	Number of data n	1,1-DCE zero-time intercept ( $\mu\text{g/L}$ )	$k_e$ ( $\text{yr}^{-1}$ )
Control	19	$15.5 \pm 1.8$	$0.040 \pm 0.004$
Acetone/2-propanol	19	$13.6 \pm 2.6$	$0.037 \pm 0.006$
Acetone/2-propanol/ $\text{HgCl}_2$	19	$12.3 \pm 1.8$	$0.044 \pm 0.006$
All data (normalized)	57		$0.040 \pm 0.003$

<sup>a</sup>  $\pm$  values represent 95% confidence intervals.



water without  $\text{HgCl}_2$  and 2 with  $\text{HgCl}_2$  added were analyzed for a range of chlorinated products. TCA was found to decrease from an average initial value of  $132\text{ }\mu\text{g/L}$  to an average of  $109\text{ }\mu\text{g/L}$ , and an average of  $4.3\text{ }\mu\text{g/L}$  of 1,1-DCE was formed. No other chlorinated products were detected by any of the three GC techniques used. All three procedures, including GC/MS, indicated the product formed was 1,1-DCE. The calculated rate constant,  $k_e$ , for 1,1-DCE formation from TCA was  $0.04\text{ yr}^{-1}$ , which is in agreement with the previous study results.

A mass balance for TCA and 1,1-DCE did not account for 74% of the TCA concentration decrease during the 380 days of incubation. This loss might be associated either with formation of decomposition products other than 1,1-DCE, e.g., acetic acid (T. Mill, pers. commun., 1986), with analytical errors, or with loss of TCA and 1,1-DCE from the sample bottles during the long storage period. In any event, the mass balance is consistent with a half-life from TCA in excess of 3 yrs under the experimental conditions used. This is also in agreement with the initial study results.

## DISCUSSION

This study confirms that 1,1-DCE is formed from the abiotic dehydrochlorination of TCA in dilute aqueous solutions at neutral pH and  $20^\circ\text{C}$ , conditions common in groundwater environments. From the extension study of groundwaters in the United States (Westrick et al., 1984), 1,1-DCE was found in detectable concentrations about one-third as frequently as TCA. In addition, a co-occurrence study of these results indicated that TCA was also observed in 67% of the groundwater samples where 1,1-DCE was found (Price, 1985). This study indicates some of the 1,1-DCE detected may have resulted from TCA transformation. Although the formation rate of 1,1-DCE is relatively low, residence times of groundwaters are relatively long. Within a few years, significant concentrations of 1,1-DCE could result from TCA abiotic transformation.

1,1-DCE might not be the only product resulting from abiotic transformation of TCA. While no other confirmed products were detected in this study, analyses were not conducted for acetic acid, which has been reported as a product (Britton and Reed, 1932; Walraevens et al., 1974; Mabey et al., 1983). If 1,1-DCE were the only product of abiotic TCA transformation under the conditions studied, then the TCA half-life could be inferred from the measured constant  $k_e$ . This would be 17 yrs based on an average  $k_e$  value of  $0.040\text{ yr}^{-1}$ . Considering the 95% confidence intervals for the pooled 1,1-DCE data, the shortest half-life would be 16 yrs and the longest 19 yrs.

If TCA decomposed to form products in addition to 1,1-DCE, such as acetic acid (eqn 1), then the overall rate of TCA decomposition would be greater than that given by  $k_e$  alone. The TCA concentration measurements and time scale of the experiments were not adequate to obtain a precise direct measurement of TCA loss. However, they were sufficient to put bounds on the rate. Using the outer bound indicating the most rapid decomposition rate at the 95% confidence limit for the pooled data, a minimum half-life for TCA under the experimental conditions studied would be 2.8 yrs.

At the other extreme, if 1,1-DCE were the only product, then the maximum half-life for TCA would be indicated by the 95% confidence interval associated with the minimum formation rate of 1,1-DCE. This half-life is 19 yrs. Thus, the half-life for abiotic decomposition of TCA from this study lies between 2.8 and 19 yrs in dilute aqueous solutions at neutral pH and 20°C.

The TCA half-life represented by the range determined in this study is longer than the half-life of 1.4 yrs that has been estimated (at 20°C) from extrapolation of higher-temperature experimental data (Mabey et al., 1983), and is also considerably higher than values of 0.5 yrs at 25°C in distilled water reported by Dilling et al. (1975) and 0.8 yrs in sea water at 10°C and pH 8 reported by Pearson and McConnell (1975). Reasons for the discrepancies are not evident although experimental procedures differed significantly. In addition, the abiotic transformation rates in groundwater environments may differ from those measured in homogeneous solutions. Little is known about the effects of sorption on mineral surfaces on transformation rates. While sufficiently precise kinetic measurements are difficult to make for reactions that are very slow, it is nevertheless important that they be obtained for environmental conditions of importance. These data are necessary in order to understand the dimensions of a groundwater contamination problem, and to develop technically and economically sound control strategies.

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