(H)

59078

An Overview of Anaerobic Transformation of Chlorinated Solvents

Perry L. McCarty
Department of Civil Engineering, Stanford University, Stanford, CA

Abstract

Intrinsic cometabolic transformation of chlorinated solvents commonly occurs at sites where co-contaminants are present as primary substrates to support the energy needs and metabolic activities of transforming bacteria. The extent of transformation that occurs depends upon the relative concentration of primary substrates and the microorganisms and environmental conditions present. Reduction of tetrachloroethene (PCE) and trichloroethene (TCE) to ethene has occurred at many sites, although transformations are often not complete. Evidence for intrinsic biotransformation of chlorinated aliphatic hydrocarbons (CAHs) is provided by the presence of CAH transformation products and indicators of anaerobic biogical activity, such as the disappearance of dissolved oxygen, nitrates, and sulfates, and the production of methane and soluble iron (II).

Introduction

Chlorinated solvents and their natural transformation products represent the most prevalent organic ground-water contaminants in the country. These solvents, consisting primarily of CAHs, have been used widely for degreasing of aircraft engines, automobile parts, electronic components, and clothing. Only during the past 15 years has it become recognized that CAHs can be transformed biologically (1). Such transformations sometimes occur under the environmental conditions present in an aquifer in the absence of planned human intervention, a process called intrinsic biotransformation (2). Conditions under which this is likely to occur with CAHs and the end products that can be expected are discussed in this paper.

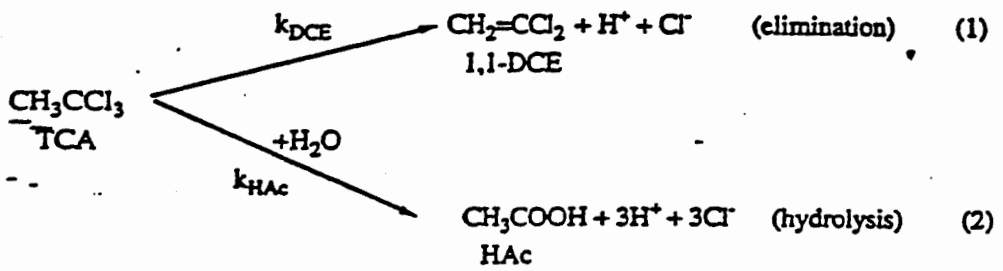
The major chlorinated solvents are carbon tetrachloride (CT), PCE, TCE, and 1,1,1-trichloroethane (TCA). These compounds can be transformed by chemical and biological processes in soils to form a variety of other CAHs, including chloroform (CF), methylene chloride (MC), cis- and trans-1,2-dichloroethene (c-DCE, t-DCE), 1,1-dichloroethene (1,1-DCE), vinyl chloride (VC), 1,1-dichloroethane (DCA), and chloroethane (CA). In CAH transformation, the microorganisms responsible cannot obtain energy for growth from the transformations. The transformations are brought about through co-metabolism or through interactions of the CAHs with enzymes or cofactors produced by the microorganisms for other purposes. In co-metabolism, other organic chemicals must be present to serve as primary substrates to satisfy the energy needs of the microorganisms. Chemical transformations of some CAHs can also occur within the timeframe of interest in ground water. Transformations that are likely, and the environmental conditions required, are discussed below.

Received by ER-RPF
SEP 04 1998
MA

7186

Chemical Transformation

TCA is the only major chlorinated solvent that can be transformed chemically in ground water under all conditions likely to be found and within the one- to two-decade time span of general interest, although chemical transformation of CT through reductive processes is a possibility. TCA chemical transformation occurs by two different pathways, leading to the formation of 1,1-DCE and acetic acid (HAc):



The rate of each chemical transformation is given by the first-order reaction:

$$C = C_o e^{-kt} \qquad (3)$$

where C is the concentration of TCA at any time t, C_o represents the initial concentration at t = 0, and k is a transformation rate constant. The overall rate constant for TCA transformation (kTCA) is equal to the sum of the individual rate constants ($k_{DCE} + k_{HAc}$). The transformation rate constants are functions of temperature:

$$k = Ae^{-E/0.008314K} \qquad (4)$$

where A and E are constants and K is the temperature in degrees Kelvin. Table 1 provides a listing of values reported for A and E for TCA abiotic transformation by various investigators, and calculated values for the TCA transformation rate constant for 10°C, 15°C, and 20°C using equation 4. Also given is the average calculated TCA half-life based upon t1/2 = 0.69/k. The temperature effect on TCA half-life is quite significant.

Table 1. Reported First-Order TCA Abiotic Transformation Rates (k_{TCA})

A yr^{-1}	E kJ	k_{TCA} (yr^{-1}) 10 °C	15 °C	20 °C	References
3.47 $(10)^{20}$	118.0	0.058	0.137	0.32	Haag and Mill (3)
6.31 $(10)^{20}$	119.3	0.060	0.145	0.34	Cline and Delfino (4)
1.56 $(10)^{20}$	116.1	0.058	0.137	0.31	Jeffers et al. (5)
Average half-life (yr)		12	4.9	0.95	

Cline and Delfino (4) found that k_{DCE} equaled about 21 percent of K_{TCA}, and Haag and Mill (3) found it to be 22 percent. This means that almost 80 percent of the TCA is transformed into acetic acid. The 20-plus percent that is converted to 1,1-DCE, however, is of great significance because 1,1-DCE is considered more toxic than TCA, with a maximum contaminant level of 7 μg/L compared with 200 μg/L for TCA. Whenever TCA is present as a contaminant, 1,1-DCE can also be expected. In general, TCA is probably the main source of 1,1-DCE contamination found in aquifers.

Chloroethane, formed through biological transformation of TCA, can also be chemically transformed with a half-life on the order of months by hydrolysis to ethanol, which can then be biologically converted to acetic acid and nonharmful products (6).

Biological Transformations

CAHs can be oxidized or reduced, generally through co-metabolism, as noted in Table 2. In ground waters, intrinsic reductive transformations are most often noted, perhaps because the presence of intermediate products that are formed provide strong evidence that reductive transformations are taking place. Intrinsic aerobic transformation of TCE is also possible, although if it did occur, the intermediate products are unstable and more difficult, analytically, to measure. Thus, convincing evidence for the latter is difficult to obtain. Also, aerobic co-metabolism of TCE would only occur if sufficient dissolved oxygen and a suitable electron donor, such as methane, ammonia, or phenol, were present. Since circumstances under which the proper environmental conditions for significant aerobic co-metabolism are unlikely to occur often, intrinsic aerobic co-metabolism of TCE is probably of little significance. Evidence is ample, however, that anaerobic reductived transformations of CAHs occur frequently, and this process is important to the transformation of all chlorinated solvents and their transformation products. The major environmental requirement is the presence of sufficient concentrations of other organics that can serve as electron donors for energy metabolism, which often is the case in aquifers. Indeed, the extent to which reductive dehalogenation occurs may be limited by the amount of such co-contaminants present. Theoretically, only a 0.4-g chemical oxygen demand (COD) equivalent of primary substrate would be required to convert 1 g of PCE to ethene (7), but much more is actually required because of the co-metabolic nature of the transformation.

Figure 1 illustrates the potential chemical and biological transformation pathways for the four major chlorinated solvents under anaerobic environmental conditions (6). Freedman and Gossett (8) provided the first evidence for conversion of PCE and TCE to ethene, and de Bruin et al. (9) reported completed reduction to ethane. Table 3 indicates that while some transformations, such as CT to chloroform and carbon dioxide, may take place under mild reducing conditions such as those associated with denitrification, complete reductive transformation to inorganic end products and of PCE and TCE to ethene generally requires conditions suitable for methane fermentation. Extensive reduction, although perhaps not complete, can also occur under sulfate-reducing conditions. For methane fermentation to occur in an aquifer, the presence of sufficient organic co-contaminant is required to reduce the oxygen, nitrate, nitrite, and sulfate present. Some organics will be required to reduce the CAHs, and perhaps Fe(II) as well, if present in significant amounts. If the potential for intrinsic transformation of CAHs is to be evaluated, then the concentrations of nitrate, nitrite, sulfate, Fe(II), and methane, and of organics (as indicated by COD or total organic carbon [TOC]) should be determined. Unfortunately, such analyses are not considered essential in remedial investigations, but it is evident that they should be.

Table 2. Biodegradability of Chlorinated Solvents Under Aerobic or Anaerobic Conditions and Through Use as a Primary Substrate for Energy and Growth or Through Co-metabolism

	Carbon Tetrachloride (CT)	Tetrachloro-ethylene (PCE)	Trichloro-ethylene (TCE)	1,1,1-Tri-chloroethane (TCA)
Aerobic Biotransformation				
Primary substrate	No	No	No	No
Co-metabolism	No	No	Yes	Perhaps
Anaerobic Biotransformation				
Primary substrate	No	Perhaps	Perhaps	No
Co-metabolism	Yes	Yes	Yes	Yes
Hazardous intermediates	Yes	Yes	Yes	Yes
Chemical Transformation	Perhaps	No	No	Yes

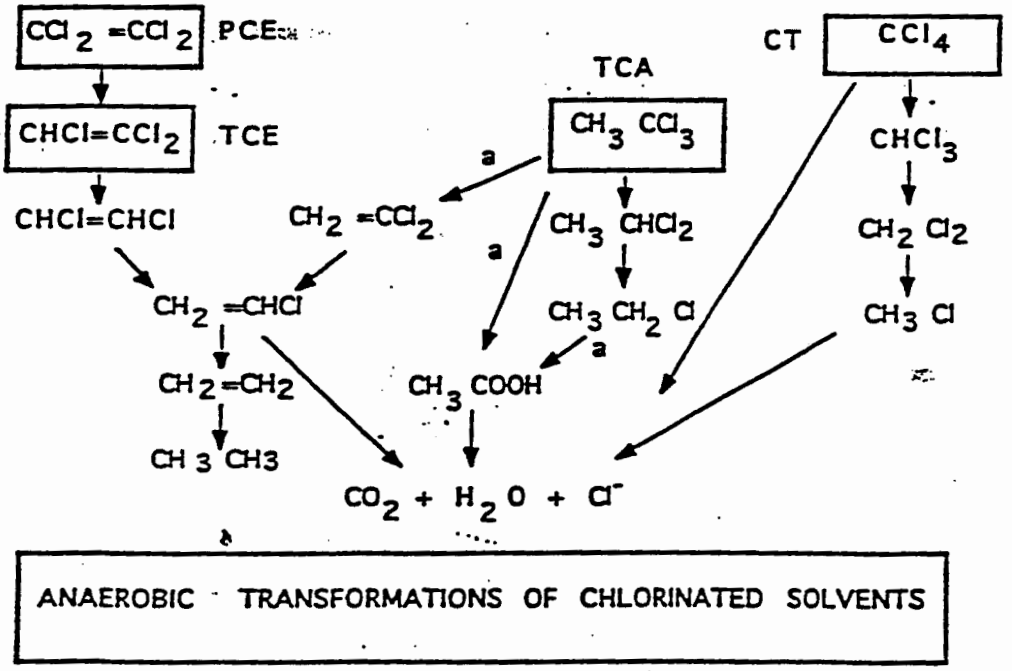


Figure 1. Anaerobic chemical and biological transformation pathways for chlorinated solvents.

Table 3. Environmental Conditions Generally Associated With Reductive Transformations of Chlorinated Solvents

	Redox Environment			
Chlorinated Solvent	All	Denitrification	Sulfate Reduction	Methanogenesis
Carbon tetrachloride		CT→CF	CT→CO_2+Cl^-	
1,1,1-Trichloroethane	TCA→1,1-DCE + CH_3COOH		TCA→1,1-DCA	TCA→CO_2+Cl^-
Tetrachloroethylene			PCE→1,2-DCE	PCE→ethene
Trichloroethylene			TCE→1,2-DCE	TCE→ethene

Case Studies

Major et al. (10) reported field evidence for intrinsic bioremediation of PCE to ethene and ethane at a chemical transfer facility in North Toronto. PCE was stored at the site 10 years prior to the study and contaminated the ground water below with both free and dissolved PCE. In addition to high concentrations of PCE (4.4 mg/L), high concentrations of methanol (810 mg/L) and acetate (430 mg/L) were found in the contaminated ground water; methanol and acetate are co-contaminants that served as the primary substrates for the transforming organisms. Where high PCE was found, TCE (1.7 mg/L), cis-DCE (5.8 mg/L), and VC (0.22 mg/L) were also found, but little ethene (0.01 mg/L) was found. At one downgradient well, however, no PCE or TCE was found, but cis-DCE (76 mg/L), VC (9.7 mg/L), and ethene (0.42 mg/L) were present, suggesting that significant dehalogenation had occurred. Other dichloroethylenes (1,1-DCE and trans-DCE) were not significant in concentration, indicating that cis-DCE was the major transformation intermediate. Microcosm studies also supported that biotransformation was occurring at the site, with complete disappearance of PCE, TCE, and cis-DCE and production of both VC and ethene. The conversions were accompanied by significant methane production, indicating that suitable redox conditions were present for the transformation.

Fiorenza et al. (11) reported on PCE, TCE, TCA, and dichloromethane (DCM) contamination of ground water at two separate locations at a carpet-backing manufacturing plant in Hawkesbury, Ontario. The waste lagoon was the major contaminated area, with ground water containing 492 mg/L of volatile fatty acids and 4.2 mg/L of methanol, organics that appeared to provide the co-contaminants that served as primary sources of energy for the dehalogenation reactions. Here, the sulfate concentration was nondetected, but the concentration in native ground water was about 15 to 18 mg/L. Total dissolved iron was quite high (19.5 mg/L) and well above the upgradient concentration of 2.1 mg/L. Methane was present, although quite low in concentration (0.06 mg/L). These parameters are all supportive of conditions suitable for intrinsic biodegradation of the chlorinated solvents. While some chemical transformation of TCA was indicated (0.4 mg/L), biotransformation was quite extensive, as indicated by a 1,1-DCA concentration of 7.2 mg/L compared with the TCA concentration of 5.5 mg/L. Some CA was also present (0.19 mg/L). Transformation was also indicated for PCE and TCE, which remained at concentrations of only 0.016 mg/L and 1.5 mg/L, respectively, while the cis-DCE, VC, and

ethene concentrations were 56, 4.2, and 0.076 mg/L, respectively. Only traces of ethane were found. Trans-DCE concentration was only 0.57 mg/L, again providing evidence that cis-DCE is the most common transformation intermediate from TCE and PCE. Downgradient from the lagoon, the dominant products were cis-DCE (4.5 mg/L), VC (5.2 mg/L), and 1,1-DCA (2.1 mg/L). While good evidence for intrinsic biotransformation is provided for this site, the ethene and ethane concentrations appear very low compared with VC concentration, suggesting that biotransformation was not eliminating the chlorinated solvent hazard at the site, although it was producing compounds that may be more susceptible to aerobic co-metabolism.

Evidence for intrinsic biotransformation of chlorinated solvents has also been provided from analyses of gas from municipal refuse landfills where active methane fermenation exists. A summary by McCarty and Reinhard (12) of data from Chamley et al. (13) indicated average gaseous concentrations in parts per million by volume from eight refuse landfills to be: PCE, 7.15; TCE, 5.09; cis-DCE, not measured; trans-DCE, 0.02; and VC, 5.6. While these averages indicate that, in general, transformation was not complete, the presence of high VC indicates the transformation was significant. For TCA, gaseous concentrations were: TCA, 0.17; 1,1-DCE, 0.10; 1,1-DCA, 2.5; and CA, 0.37. These data indicate that TCA biotransformation was quite extensive, with the transformation intermediate, 1,1-DCA, present at quite significant levels, as is frequently found in ground water.

Perhaps the most extensively studied and reported intrinsic chlorinated solvent biodegradation is that at the St. Joseph, Michigan, Superfund site (7, 14-17). Ground-water concentrations of TCE as high as 100 mg/L were found present, with extensive transformation to cis-DCE, VC, and ethene. A high but undefined COD (400 mg/L) in ground water, resulting from waste leaching from a disposal lagoon, provided the energy source for the co-metabolic reduction of TCE. Nearly complete conversion of the COD to methane provided evidence of the ideal conditions for intrinsic bioremediation (7). Extensive analysis near the source of contamination indicated that 8 percent to 25 percent of the TCE had been converted to ethene, and that up to 15 percent of the reduction in COD in this zone was associated with reductive dehalogenation (15). Through more extensive analysis of ground water farther downgradient from the contaminating source, Wilson et al. (17) found a 24-fold reduction in CAHs across the site. A review of the data at individual sampling points indicated that conversion of TCE to ethene was most complete where methane production was highest and removal of nitrate and sulfate by reduction was most complete.

References

1. McCarty, P.L., and L. Semprini. 1994. Ground-water treatment for chlorinated solvents. In: Norris, R.E., ed. Handbook of bioremediation. Boca Raton, FL: Lewis Publishers, Inc. pp. 87-116.

2. Council, N.R. 1993. *In situ* bioremediation: When does it work?. Washington, DC: National Academy Press.

3. Haag, W.R., and T. Mill. 1988. Effect of subsurface sediment on hydrolysis of haloalkanes and epoxides. Environ. Sci. Technol. 22:658-663.

4. Cline, P.V., and J.J. Delfino. 1989. Transformation kinetics of 1,1,1-trichloroethane to the stable product 1,1-dichloroethene. In: R.A. Larson, ed. Biohazards of drinking water treatment. Chelsea, MI: Lewis Publishers, Inc. pp. 47-56.

5. Jeffers, P., L. Ward, L. Woytowitch, and L. Wolfe. 1989. Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propanes. Environ. Sci. Technol. 23(8): 965-969.

6. Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21:722-736.

7. McCarty, P.L., and J.T. Wilson. 1992. Natural anaerobic treatment of a TCE plume, St. Joseph, Michigan, NPL site. In: U.S. EPA. Bioremediation of hazardous wastes. EPA/600/R-92/126. Cincinnati, OH. pp. 47-50.

8. Freedman, D.L., and J.M. Gossett. 1989. Biological reductive dechlorination of tetrachloroethylene and trichloroethylene to ethylene under methanogenic conditions. Appl. Environ. Microbiol. 55(9):2,144-2,151.

9. de Bruin, W.P., et al. 1992. Complete biological reductive transformation of tetrachloroethene to ethane. Appl. Environ. Microbiol. 58(6):1,996-2,000.

10. Major, D.W., W.W. Hodgins, and B.J. Butler. 1991. Field and laboratory evidence of *in situ* biotransformation of tetrachloroethene to ethene and ethane at a chemical transfer facility in North Toronto. In: Hinchee, R.E., and R.F. Olfenbuttel, eds. Onsite bioreclamation. Boston, MA: Butterworth-Heinemann. pp. 147-171.

11. Fiorenza, S., et al. 1994. Natural anaerobic degradation of chlorinated solvents at a Canadian manufacturing plant. In: Hinchee, R.E., A. Leeson, L. Semprini, and S.K. Ong, eds. Bioremediation of chlorinated and polycyclic aromatic hydrocarbon compounds. Boca Raton, FL: Lewis Publishers, Inc. pp. 277-286.

12. McCarty, P.L., and M. Reinhard. 1993. Biological and chemical transformations of halogenated aliphatic compounds in aquatic and terrestrial environments. In: Oremland, R.S., ed. The biogeochemistry of global change: Radiative trace gases. New York, NY: Chapman & Hall, Inc.

13. Charnley, G., E.A.C. Crouch, L.C. Green, and T.L. Lash. 1988. Municipal solid waste landfilling: A review of environmental effects. No. Meta Systems, Inc.

14. Haston, Z.C., P.K. Sharma, J.N. Black, and P.L. McCarty. 1994. Enhanced reductive dechlorination of chlorinated ethenes. In: U.S. EPA. Bioremediation of hazardous wastes. San Francisco, CA.

15. Kitanidis, P.K., L. Semprini, D.H. Kampbell, and J.T. Wilson. 1993. Natural anaerobic bioremediation of TCE at the St. Joseph, Michigan, Superfund site. In: U.S. EPA. Symposium on bioremediation of hazardous wastes: Research, development, and field evaluations (abstracts). EPA/600/R-93/054. Washington, DC (May). Cincinnati, OH. pp. 47-50.

16. McCarty, P.L., et al. 1991. *In situ* methanotrophic bioremediation for contaminated ground water at St. Joseph, Michigan. In: Hinchee, R.E., and R.G. Olfenbuttel, eds. Onsite bioreclamation processes for xenobiotic and hydrocarbon treatment. Boston, MA: Butterworth-Heinemann. pp. 16-40.

17. Wilson, J.T., J.W. Weaver, and D.H. Kampbell. 1994. Intrinsic bioremediation of TCE in ground water at an NPL site in St. Joseph, Michigan. Presented at the U.S. EPA Symposium on Intrinsic Bioremediation of Ground Water, Denver, CO (August 30 to September 1).