The Vinyl Institute

REV 8(E)

TECHNICAL INFORMATION

ON THE POTENTIAL SOURCES OF VINYL CHLORIDE IN LANDFILLS AND GROUNDWATER

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Issued: March 1990

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INTRODUCTION

Within the past decade, numerous reports have appeared in the media which have spotlighted the identification of volatile organic chemicals (VOC's) in groundwater and drinking water supplies. In some cases, the origin of the VOC's could be inferred from the proximity of industrial or commercial facilities when their use or disposal practices were taken into account. In other cases, however, no obvious connection was discernible between the appearance of specific chemical compounds in a given location and their use or disposal in that area (9, 13, 14). It is this particular dilemma that is the subject of this paper.

A number of authors and agencies have concerned themselves with the occurrence of vinyl chloride in groundwater, drinking water, and gas and leachate from landfills (9, 13, 19). In their efforts to discover the source or sources of the vinyl chloride being detected, the investigators have attempted to identify and examine the known and the most plausible origins as well as some which are only minor or remote possibilities. This paper, based on a review of published literature, briefly reviews the results of these examinations in an attempt to understand the issue and hopefully alleviate some unfounded concerns. Among the potential origins of vinyl chloride examined in the most complete reviews of this subject are:

- Microbial transformation of chlorinated solvents
- Chemical transformation of chlorinated solvents
- Leaching of residual vinyl chloride monomer from "old" polyvinyl chloride (PVC)
- Degradation/depolymerization of PVC
- Other sources

A list of the commonly used abbreviations for the chemical species discussed in this work is given in Table 1.

TABLE 1

Abbreviations For Chemical Species

CA - Chloroethane

DCA - Dichloroethane (1,1-)

DCE - Dichloroethene (cis, trans)

EDC - Dichloroethane (1,2-)

PCE - Tetrachloroethene (perchlorethylene or tetrachloroethylene)

TCA - Trichloroethane (1,1,1-)

TCE - Trichloroethene

VC - Chloroethene (vinyl chloride)

VDC - Vinylidene Chloride (1,1-dichloroethene)

MICROBIAL TRANSFORMATION OF CHLORINATED SOLVENTS

Of the potential sources of vinyl chloride monomer in landfills and groundwater, the one origin that has been the most extensively researched and characterized is the biotransformation of chlorinated solvents under a variety of conditions.

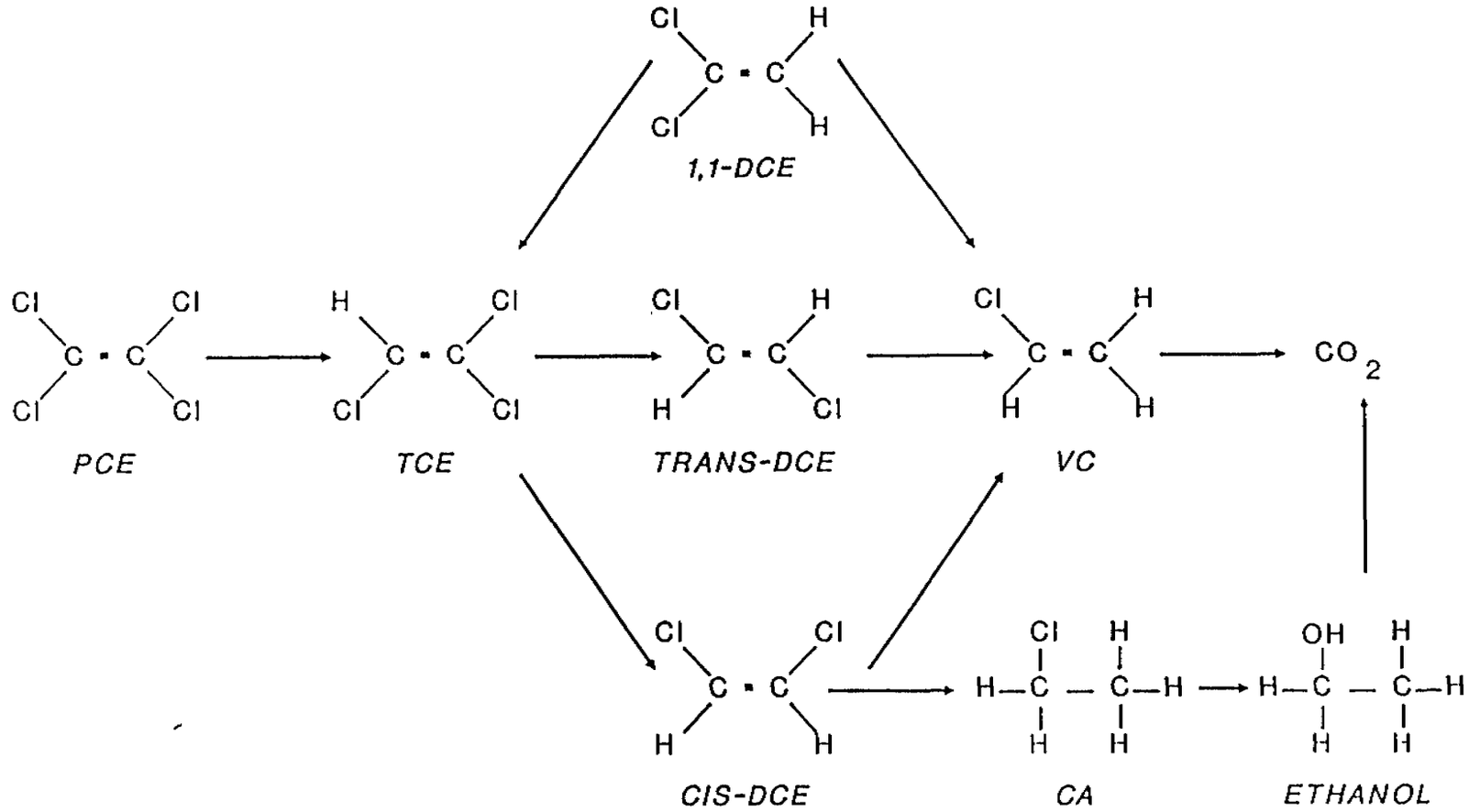
Figure 1 shows the pathways of reductive dehalogenation which lead to the biotransformation of the common chlorinated solvent perchloroethylene (PCE or tetrachloroethylene) under methanogenic conditions. In Figure 2, the pathways for the transformation of trichloroethane by both biological and abiotic means are illustrated.

Early work by Bouwer and McCarty (2) demonstrated that some 1- and 2- carbon halogenated aliphatic compounds could be degraded under methanogenic conditions in the laboratory. This work suggested the existence of a sequential pathway for the degradation, as mixed cultures seeded with PCE and incubated for 8 weeks under methanogenic conditions produced measurable amounts of trichloroethylene (TCE). Parsons et al (10, 11) conducted studies in static microcosms and groundwater which demonstrated the ability of micro-organisms in muck from an aquifer recharge basin to transform PCE and TCE to cis and trans 1,2-dichloroethylene (cis-DCE and trans-DCE) and vinyl chloride (VC). No such transformation occurred when the muck material was sterilized before incubation. This study suggested how the cis and trans dichloroethylene and vinyl chloride could be found in groundwater in an area where these materials had not been used and yet PCE, TCE and TCA were widely used (13, 14).

Additional studies by Kleopfer et al (8) and Barrio-Lage et al (1) as well as others (3, 4, 12, 15, 16, 17, 18) have solidly established the ability of microbial cultures in methanogenic environments to transform the most commonly found chlorinated solvents (PCE, TCE and TCA) to the less commonly found chemical species (cis-DCE, trans-DCE, 1,1-DCA and vinyl chloride). Even further, work by Vogel and McCarty (16) has suggested that mineralization of the VC CO_2 is possible under anaerobic conditions, Hartman et al (6) isolated a strain of Mycobacterium which could use vinyl chloride as the sole carbon and energy source for growth under aerobic conditions.

FIGURE 1

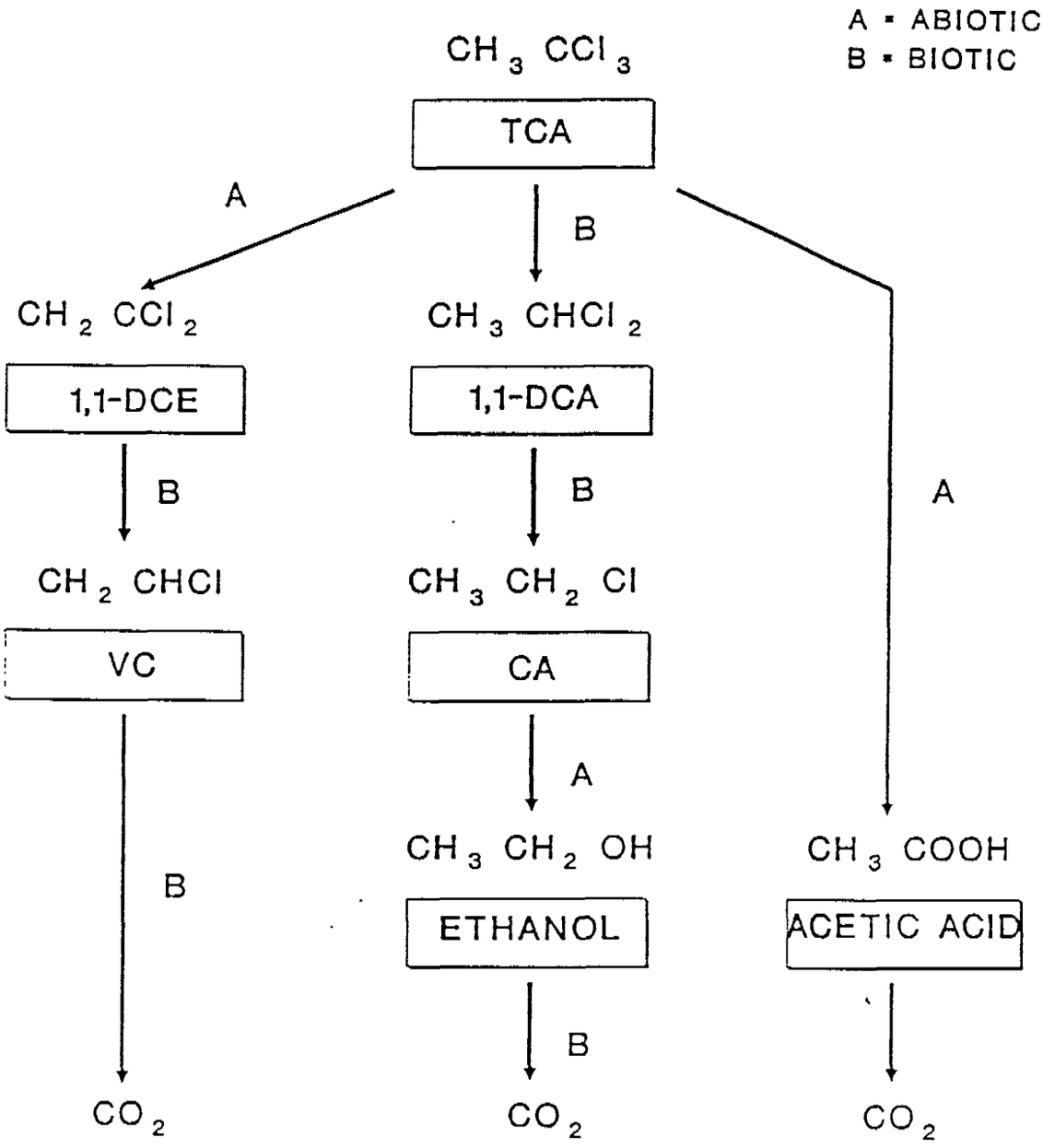
REDUCTIVE DEHALOGENATION PATHWAYS OF CHLORINATED ETHENES*



*REFERENCES 1, 2, 10, 15, 16, 17

FIGURE 2

PATHWAYS FOR THE TRANSFORMATION OF TRICHLOROETHANE UNDER METHANOGENIC CONDITIONS*



*REFERENCES 15, 17

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Finally, in their study targeted specifically at the formation of vinyl chloride in California landfills, Molten, et al (9) used samples taken from landfills known to product vinyl chloride to start an anaerobic chemostat which used methanol as the sole carbon source. They showed when the culture was incubated with 13_c labeled TCE that 13_c labeled vinyl chloride was produced. Their experiments and examinations of other sources lead them to conclude that "microbial action on chlorinated solvents in landfills is the most probable source of observed VC (vinyl chloride) formation in situ."

All of the foregoing strongly support the hypothesis that the biotransformation of chlorinated solvents in landfills and aquifers, under methanogenic conditions can lead to the formation of vinyl chloride and is an important potential source of this material in the environment. However, the studies also point out that variations in microbial flora, chlorinated substrate, and the presence of alternative carbon sources are likely to influence both the pathways and the rate of formation of specific compounds. In addition, actions taken by manufacturers and users of chlorinated solvents as well as efforts by regulatory agencies have served to eliminate landfills as major disposal routes.

CHEMICAL TRANSFORMATION OF CHLORINATED SOLVENTS

A recent and complete review of the abiotic transformation of halogenated aliphatic compounds has been published by Vogel, et al (15). In their work, the authors point out that although most abiotic transformations are slow when compared with biotic transformations, they can still be significant within the time scales associated with groundwater movement. They concluded that the most likely transformations under a given set of conditions is strongly influenced by the number and type of halogen substituents, with oxidation and reduction reactions being favored as halogen numbers increased.

Tabulated reaction products for systems involving chlorinated ethanes included ethanol, acetic acid, 1,1-DCE, TCE and CO_2. Figure 2 illustrates the nature of abiotic steps in the transformation of TCA. In the same study (15), these authors reported the stoichiometry of the conversion of 1,1-DCE to VC and partial mineralization to CO_2. The overall fate of TCA (i.e., reaction rates, intermediates, etc.) is largely influenced by environment, microbial flora and organic content. Therefore, the consumption of precursors to vinyl chloride by alternate and even favored routes should be considered. An example would be the rapid conversion of TCA in anaerobic conditions to 1,1-DCA and further to CO_2 versus the alternative route to VC (Figure 2). Vogel et al (15) concluded that the products and complex pathways of Figure 2 were consistent with field observations of products found in groundwaters contaminated with 1,1,1-TCA. An additional analysis (19) of abiotic steps in the transformation of TCA to lesser chlorinated species including VC concluded that thermodynamic factors did not favor the reactions directly leading to VC and that activation energies associated with others would provide formidable barriers to reaction. Bacterial, chemical and thermal catalytic effects could overcome the barriers, however, so chemical transformations were at least possible.

The overall conclusion that can be drawn from the work done in this area is that some contribution to the degradation products detected is probably of abiotic origin. The magnitude of the contribution is expected to be small relative to biotransformation when thermodynamic and kinetic effects are taken into account. Other experimental evidence suggests agreement with this conclusion. As noted above, Figure 2 illustrates abiotic and biotic pathways for the transformation of TCA through a variety of intermediates to carbon dioxide.

LEACHING OF RESIDUAL VINYL CHLORIDE FROM "OLD" PVC

It is generally acknowledged that PVC produced before 1975 was likely to contain higher levels of residual monomer than PVC produced since then. Levels as high as 330 ppm of residual monomer have been reported for old material, whereas less than 3 ppm is now typical of material produced within the last 10 years. Sites which have received PVC waste sludges from industrial concerns in the past could have had some contribution to detected VC (9). The contribution, however, is probably minor given the non-linear equilibrium distribution of VC between PVC powder and water and the elevated subsurface temperatures of landfills. It has been suggested (9) that sludges with high initial VC content and surface area would desorb rapidly into the aqueous phase and further into the air by other interactions. This could account for an initial contribution but would be unlikely to contribute significantly after 1 or 2 years.

As has been pointed out, the continued appearance of VC above landfills fully 10 years after the dumping of sludges ceased argues against a major contribution by this route over a long period of time. Additionally, it should be recognized that the occurrence of VC in the absence of chlorinated solvents is virtually unknown.

DEGRADATION/DEPOLYMERIZATION OF PVC

In the aftermath of the first discoveries of vinyl chloride being emitted from landfills and detected in groundwater, any and all potential sources were identified with little regard for level of contribution or experimental evidence. This appears to have been the case with the depolymerization of PVC.

The thermal, photolytic, biological and high energy degradation paths of PVC have been examined (7, 9 and references therein). Pyrolysis experiments on PVC at temperatures from 150°C to 650°C released expected amounts of residual monomer, but no formation of new monomer was detected (9). The expected products, HCl and hydrocarbons from the known decomposition route were detected. Earlier research has reported a maximum of 35 ppm VC detected from PVC pyrolysis in air at 350°C and a maximum of 6 ppm was found at 500°C in a helium atmosphere. With only these minor levels of production, and the temperatures required, it can be calculated that a vast majority of the carbon present in a landfill would have to be present as PVC for this mechanism to produce the observed levels of VC at many landfills. Since it is well known (5) that plastics in general only constitute approximately 7% of landfill contents and PVC is less than 10% of that amount, thermal degradation of PVC is very improbable as a source of VC in landfills.

Other routes of PVC degradation, photolytic and high energy, have been shown to be even less likely given the presence of soil covers and the absence of high energy source. The only remaining degradation route, biological, is strongly argued against by the myriad of applications of PVC articles in above and below ground applications. It is the well characterized resistance of this material to aggressive environments that makes it a desirable material of construction. As an example of this, the Uni-Bell PVC Pipe Association of Dallas, Texas, recently completed some pipe longevity research in which a 200 foot section (out of 250,000 feet) of 4" diameter PVC water pipe was unearthed after 22 years in undisturbed underground service. The measurements and tests performed on the pipe showed that it met or exceeded the standards for new pipe in every respect. Unlike other polymers, PVC is not known to depolymerize or "unzip" with release of monomer (7).

The above discussion and the absence from the literature of any documentation of significant PVC depolymerization to monomer argues strongly that depolymerization is not a significant source of detected VC in the environment.

OTHER SOURCES

Several other potential sources of VC have been identified including the release of VC used as a propellant in old aerosol cans and legal or illegal dumping of PVC production sludges.

The use of VC as a propellant in aerosol products was banned in 1974. Release of residual propellant due to corrosion or crushing in landfill sites. However, this source offers no explanation for VC detected remote from landfill sites, associated with aquifers, or where chlorinated solvents are known to have been spilled. The overall contribution has been judged to be minor (9, 19).

Disposal practices in the past involving PVC production sludges could have accounted for some emissions of VC from landfills known to have accepted such materials or suspected of having received them illegally. However, such sludges cannot be used as an explanation for the detection of VC over landfills which have never received such materials or where chlorinated solvents have also been detected such as in spill or leakage sites. Sludges taken from specific landfill sites in California (9) tend to support this conclusion.

Given the high vapor pressure (2964 mm Hg at 25°C) and low boiling point of (-13.8°C) of vinyl chloride introduction of this material to surface soils or waters will usually result in rapid volatilization and would be an unlikely source of groundwater contamination.

CONCLUSIONS

The result of scientific investigations reviewed here support the following conclusions regarding the occurrence of vinyl chloride in landfills or groundwater:

1. The decomposition of polyvinyl chloride plastics (PVC) is the least probable source of vinyl chloride.

2. The biotransformation of perchloroethylene to trichloroethylene, dichloroethylene, vinyl chloride and carbon dioxide has been demonstrated (figures 1 and 2). Thus, the microbial decomposition of chlorinated hydrocarbons may include the transient formation of a variety of intermediates as they are ultimately mineralized to carbon dioxide.

3. The abiotic transformation of chlorinated hydrocarbons may contribute minor amounts of vinyl chloride that may subsequently undergo biotransformations to carbon dioxide (Figure 2).

4. Several other potential sources of vinyl chloride include the release of vinyl chloride gas historically used as a propellant in aerosol cans placed in landfills and past practice of land disposal of polyvinyl chloride (PVC) sludges.

5. It is reasonable to expect vinyl chloride to undergo decomposition to carbon dioxide regardless of the source.

6. Actions taken by manufacturers and users of chlorinated hydrocarbons along with efforts by regulatory agencies have served to eliminate landfills as a major disposal route for these substances.

REFERENCES

1. Barrio-Lage, G., F.Z. Parsons, R.S. Nasser, and P.A. Lorenzo. 1986. Sequential Dehalogenation of Chlorinated Ethenes. Environ. Sci. Technology 20:96-99.

2. Bouwer, E.J. and P.L. McCarty. 1983. Transformations of 1- and 2- Carbon Halogenated Aliphatic Organic Compounds Under Methanogenic Conditions. Appl. Environ. Microbiol. 45:1286-1294.

3. Bouwer, E.J. and P.L. McCarty. 1984. Modeling of Trace Organics Biotransformation in the Subsurface. Groundwater 22:433-440.

4. Bouwer, E.J., and J.P. Wright. 1988. Transformations of Trace Halogenated Aliphatics in Anoxic Biofilm Columns. J. Contamin. Hydrol. 2:155-169.

5. Gottesman, R.T., W.F. Carroll and L. Fishbein. 1988. Vinyl Industry Response to Environmental Concerns About PVC in Municipal Solid Waste. Energy Progress. 8:148-153.

6. Hartman, S, J.A.M. deBont, J. Tramper, K. Ch. A.M. Luyben. 1985. Bacterial Degradation of Vinyl Chloride. Biotechnol. Letters 7:383-388.

7. Kirk-Othmer. Encyclopedia of Chemical Technology, Third Edition, Volume 23, Vinyl Polymers (PVC). 886-936.

8. Kleopfer, R.D., D.M. Easley, B.B. Haas, Jr., T.G. Deihl, D.E. Jackson, and C.J. Wurrey. 1985. Anaerobic Degradation of Trichloroethylene in Soil. Environ. Sci. Technol. 19:277-280.

9. Molton, P.M., R.T. Hallen, and J.W. Pyne. 1987. Study of Vinyl Chloride Formation at Landfill Sites in California. California State Air Resources Board Contract A4-154-32; NTIS PB 87-161279.

10. Parsons, F.Z., G. Barrio-Lage, and R. Rice. 1985. Biotransformation of Chlorinated Organic Solvents in Static Microcosms. Environ. Toxicol. Chem. 4:739-742.

11. Parsons, F., P.R. Wood and J. DeMarco. 1984. Transformations of Tetrachloroethene and Trichloroethene in Microcosms and Groundwater. J. Am. Water Works Association 76:56-59.

12. Sulfita, J.M. S.A. Gibson, and R.E. Beeman. 1988. Anaerobic Biotransformations of Pollutant Chemicals in Aquifers. J. Indus. Microbiol. 3:179-194.

13. U.S. EPA Contract No. 68-01-7166. Work Assignment 5, SAIC Project No. 2-813-07-545-05. Summary of Available Information Related to the Occurrence of Vinyl Chloride in Groundwater as a Transformation Product of Other Volatile Organic Chemicals. 1985.

14. Vincent, J.R. 1984. South Florida Drinking Water Investigation. Broward, Dade and Palm Beach Counties. U.S. Environmental Protection Agency, Office of Enforcement and Compliance Monitoring, National Enforcement Investigations Center. Denver, Colorado EPA-330/1-84-001.

15. Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformation of Halogenated Aliphatic Compound. Environ. Sci. Technol. 21-722-736.

16. Vogel, T.M., and P.L. McCarty. 1985. Biotransformation of Tetrachloroethylene and Trichloroethylene, Dichloroethylene, Vinyl Chloride and Carbon Dioxide Under Methanogenic Conditions. Appl. Environ. Microbiol. 49:1808-1083.

17. Vogel, T.M., and P.L. McCarty. 1987. Abiotic and Biotic Transformations of 1,1,1-Trichloroethane Under Methanogenic Conditions. Environ. Sci. Technol. 21:1208-1213.

18. Wilson, B.H., G.B. Smith and J.F. Rees. 1986. Biotransformations of Selected Alkylbenzenes and Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study. Environ. Sci. Technol. 20:997-1002.

19. Wolf, K., R. Holland and A. Rajaratnam. 1987. Vinyl Chloride Contamination: The Hidden Threat. J. Hazard Matl. 15:163-184.