(3)

59072

GROUND-WATER MICROBIOLOGY AND GEOCHEMISTRY

1993

FRANCIS H. CHAPELLE
United States Geological Survey
Columbia, South Carolina

Received by ER-RPF
SEP 0 3 1998
TM

7180

JOHN WILEY & SONS, INC.
New York / Chichester / Brisbane / Toronto / Singapore

$$1,1,1\text{-TCA} \xrightarrow{\text{Fast}} \begin{matrix} 1,1\text{-DCA} \\ 1,2\text{-DCA} \end{matrix} \xrightarrow{\text{Slow}} \text{CLA} \xrightarrow{\text{Fast}} CO_2 + H_2O$$

The interpretation that 1,1,1-TCA was transformed quickly to DCA was based entirely upon the observation that 1,1,1-TCA was largely absent in the ground water. Similarly, the interpretation that DCA was transformed slowly was based on the observed high concentrations of these compounds. Finally, the absence of CLA in downgradient areas was taken as evidence that CLA was rapidly dechlorinated.

The details of this proposed sequence are subject to criticism on the grounds that evidence for these processes independent of the water chemistry data are not provided. Broede and Passsero justified this approach based on the fact that it was the only rational alternative. Given the fact that reductive dehalogenation is so ubiquitously observed in anaerobic sediments, they argued, such evidence was not necessary. These data, however, raise questions that can only be answered by means of detailed laboratory studies. For example, the interpretation that the DCA-CLA transformation is slower than the CLA-CO_2 transformation is at variance with the observation that reductive dehalogenations tend to slow with decreasing chlorine content. It is perfectly appropriate for water chemistry data to suggest such hypotheses. However, such hypotheses would need independent verification before they could be reliably accepted.

13.3.2 In Situ Bioremediation of Chlorinated Aliphatic Compounds

Chlorinated aliphatic compounds such as TCA and TCE present special technical challenges to in situ methods of bioremediation. In the case of petroleum hydrocarbons, degradation is typically limited by the availability of appropriate electron acceptors or trace nutrients. However, under the aerobic conditions commonly encountered in shallow water-table aquifers, the degradation of alkyl halides are limited by the availability of particular degradative enzyme systems. Inducing indigenous microorganisms to produce the enzyme systems that are capable of actively degrading alkyl halides, and using this as the basis for in situ bioremediation has received considerable attention.

The most promising bioremediation strategy for alkyl halides, and the one that has attracted the most attention in recent years, is the stimulation of indigenous populations of methanotrophic bacteria with consequent induction of their methane monooxygenase enzyme systems. As MMOs are capable of gratuitously oxidizing alkyl halides, such stimulation could result in the large-scale degradation of these compounds in ground-water systems. The microbiologic basis for this has been well documented (Wilson and Wilson, 1985; Fogel, Taddeo, and Fogel, 1986); however, scaling up this process so that it can be applied to ground-water systems creates special challenges.

A field-scale evaluation of in situ bioremediation of chlorinated ethenes, which tested the feasibility of MMO induction to degrade alkyl halides, has been conducted at the Moffett Naval Air Station in California (Roberts et al., 1990; Semprini et al, 1990; Semprini et al., 1991). The hydrologic system selected for study was a shallow (4-6 meter), highly permeable (K ~ 200 ft/d) sand-gravel aquifer that

monooxygenase enzyme present in methanotrophic bacteria. Methanotrophs cannot obtain energy for growth by TCE oxidation, and methane competitively inhibits this reaction. Nevertheless, stimulation of methanotrophic activity is presently being evaluated as a potential in situ and ex situ bioremediation strategy. Under anaerobic conditions, reductive dehalogenation reactions are the most important alkyl halide-degrading processes. In electron donor-poor ground-water systems, however, reductive dehalogenations tend to be incomplete, resulting in the accumulation of vinyl chloride.

Reductive dehalogenation reactions may also be important microbial processes involved in degrading aryl halides. Unlike alkyl halides, however, aryl halides are capable of supporting the growth of heterotrophic aerobic bacteria. Consequently, aryl halides tend to be rapidly degraded in aerobic ground-water systems. While reductive dehalogenation reactions have been shown in laboratory studies to degrade halogenated benzoates, the importance of reductive dehalogenation of aryl halides in anaerobic ground-water systems is not clear. Studies have reported that dichlorobenzenes persist for long periods of time in some anaerobic ground-water systems.

Chlorinated pesticides vary widely in their susceptibility to microbial attack in ground-water systems. Some insecticides such as DDT are recalcitrant and degrade only partially. As a result of this recalcitrance, DDT has been virtually banned from agricultural practice in the United States. Herbicides such as atrazine are widely used in agricultural practice and are biodegradable in the soil zone. However, degradation rates of atrazine in nutrient-poor aquifer systems is relatively slow and appear to be limited to deethylation reactions. Thus, if rates of atrazine delivery to shallow ground-water systems exceeds rates of degradation, atrazine can accumulate in solution.

Contamination of ground-water systems by phenolic compounds is fairly common and often accompanies wood-treatment operations. Creosote, and later pentachlorophenol (PCP) were widely used as wood preservatives, and wastes from these operations often reach shallow ground-water systems. Phenolic compounds are rapidly degraded in ground-water systems under either aerobic or anaerobic conditions. The most common chlorinated phenol, pentachlorophenol, however, appears to be much more recalcitrant. Nevertheless, field evidence suggests that degradation does occur in some systems.

Available microbiologic and biochemical evidence is sufficient to explain many patterns of chlorinated hydrocarbon degradation observed in ground-water systems. However, because field conditions typically involve multiple contaminants, the presence of inhibiting chemicals or competing substrates, and other factors that make microbial processes difficult to evaluate, it is clear that much more field-oriented research is needed before a consistent picture of degradation in ground-water systems can emerge.