Biotransformation of trichloroethane (TCA) in groundwater

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ABSTRACT  Biotransformation and transport of Trichloroethane (TCA) in a saturated column has been simulated by employing a mathematical model developed by Corapcioglu et al., (1989). The model predicts the reductive dehalogenation of dissolved chlorinated aliphatics such as TCE and TCA under anaerobic conditions. The numerical results are compared with experimental data of Vogel and McCarty (1987).

INTRODUCTION

Chlorinated hydrocarbons such as TCE, PCE, TCA which are widely used in the industry, enter soils and groundwater from chemical waste disposal sites and from accidents. These types of substances are the most commonly encountered groundwater contaminants nationwide. In situ biological cleaning of contaminated aquifers is a very promising alternative due to lower clean-up costs and minimal disruption of the aquifer. Biotransformation of dissolved chlorinated hydrocarbons can provide complete mineralization to harmless end products such as CO₂. The biotransformation of chlorinated hydrocarbons such as TCA takes place in anaerobic and sometimes aerobic conditions (McCarty, 1984; Wilson et al., 1982; Wilson & Wilson, 1985). It has been observed that there are quite a number of factors affecting the rate of biotransformation of these trace organics existing as secondary substrates. These factors include, in addition to a primary substrate, inorganic nutrients such as nitrogen, phosphorus or sulfur, and required electron acceptors for oxidations. Sometimes methanogenic mixed cultures biotransform secondary substrates in the absence of oxygen. On the other hand, under anoxic conditions, some microorganisms may use nitrates or sulfates for the same purpose (McCarty, 1984). Then, in general, compounds containing two or more chlorine atoms per molecule are transformed into several intermediate compounds.

Other factors affecting biotransformation are groundwater temperature, pH, concentration of microorganisms, existence of microbiobly toxic substances, and the concentration of substrate. In addition, microorganisms might take some time for acclimation due to their initial low number. Sometimes these acclimation period may take months or years. For example, Bouwer & McCarty (1983) report 98% degradation of 1,1,1 TCE under methanogenic conditions with acetate as a primary substrate and 10 weeks of acclimation period. No biodegradation of these compounds is observed under aerobic conditions (Bouwer et al., 1981). Wilson & Wilson (1985) and Nelson et al. (1986) observed biotransformation of TCE to carbon dioxide under strictly aerobic conditions. Corapcioglu and Baehr (1987) have modeled the aerobic biodegradation of gasoline components in an unsaturated soil. They concluded that biodegradation can be substantially increased by
soil venting. Parson et al. (1984) reported the presence of cis- and trans-1,2-dichloroethane in well water at a site contaminated with trichloroethene from a leaking tank. Later, Parson & Lage (1985) have demonstrated that chlorinated alkenes were consistently more resistant to biotransformation than the chlorinated alkanes. Vogel & McCarty (1985) have clearly demonstrated that the transformation of PCE to TCE, DCE, and VC under methanogenic conditions is quantitative and this conversion process can lead to partial mineralization to CO₂. It appears that Vogel and McCarty’s data is the first experimental work showing the possible pathway for conversion of PCE to CO₂ through a reductive dehalogenation process. Barrio-Lage et al. (1986) showed similar results with experiments running up to 6 months. Furthermore, Barrio-Lage et al. (1987) reported the biotransformation of TCE to cis-1,2-dichloroethene under conditions closely representing a groundwater environment. These experiments clearly show that either in high-rate short duration artificial laboratory systems with primary substrate addition (e.g., Vogel & McCarty, 1985) or in slow rate long duration microcosms simulating in situ conditions (e.g., Kleopfer et al., 1985) TCE undergoes a reductive dechlorination process. Similar to TCE, TCA is also biotransformed to other compounds. The pathway for the biotransformation of TCA by reductive dehalogenation to 1,1-dichloroethane (1,1DCA) and chloroethane (CA) is shown in Fig. 1. Vogel & McCarty (1987) have demonstrated that this bioconversion process occurs stoichiometrically under methanogenic conditions. Replacement of a halogen (a chlorine atom) by a hydrogen atom at every step of the pathway constitutes the biotic transformation process. A fixed-film column experiment conducted by Vogel & McCarty (1987) supports the suggested pathway. Vogel & McCarty noted the rapid biotransformation of TCA to 1,1-DCA. Conversion of 1,1-DCA to CA proceeded at a much slower rate. Biotransformation data of Vogel & McCarty are shown in Fig. 2.

MATHEMATICAL MODEL

Estimating the concentration of parent and daughter compounds is an important aspect of effective groundwater management which requires the ability to predict the mass transport of contaminants under a variety of conditions. Predictions of this type are frequently facilitated by use of a mathematical model designed to represent the physical system under consideration in a simplified, but meaningful fashion. The predictive ability of such methods is based on identification and quantification of the significant physical, biological and chemical processes and construction of mathematical representations to describe these phenomena. Corapcioglu et al. (1989) have developed a mathematical model to simulate the transport and biotransformations of chlorinated hydrocarbons in groundwater. This is achieved first by defining and identifying all relevant physical, biological, and chemical processes which contribute to the fate of chlorinated hydrocarbon contaminants in a saturated porous medium and providing a conceptual framework for incorporating these processes into a mathematical formulation. The conservation principles expressed in terms of quantification of the physical, chemical, and microbial processes lead to a system of nonlinear partial differential equations governing the phenomenon.
The quantification of the bioconversion process is achieved by Michaelis-Menten kinetic equations and stoichiometric equations. Respective biotransformation rates are introduced into governing transport equations expressed in terms of molar concentrations. An approximation for one-dimensional anaerobic column experiment is then developed from the general model. A numerical solution, obtained by employing a finite difference scheme provides estimates of mole fractions. The numerical results are compared with experimental values obtained by Vogel & McCarty (1985) for biotransformation of PCE and TCE in a large anaerobic continuous column study. A schematic diagram of the mathematical model is given in Fig. 1.

**Michaelis-Menten Equations for Conversion Rates, \( M \)**

**Conservation of Mass Equations for Dissolved Compounds**

**Stoichiometric Biotransformation Equations**

- **CH\(_3\)CCl\(_3\) (TCA)**
- **CH\(_2\)CHCl\(_2\) (1,1-DCA)**
- **CH\(_2\)CH\(_2\)Cl (CA)**

**Fig. 1** Schematic diagram of the mathematical model and the pathway for biotransformation of TCA by reductive dehalogenation.

**NUMERICAL RESULTS AND CONCLUSIONS**

The model developed by Corapcioglu et al. (1989) has been applied to simulate the biotransformation of TCA along a large anaerobic fixed-film column as reported by Vogel & McCarty (1987). The operation of the column has been described by Vogel & McCarty (1985). The porosity of the column was 0.19. An influent solution containing TCA, nutrients and primary substrates was continuously fed with a superficial velocity of 33 cm/day. Samples were removed from the column through ports at different locations. Experimental data are given in percentages of influent TCA carbon. The data of Vogel & McCarty (1988) is illustrated in Fig. 2. The mathematical model was run with model parameters given in Table 1. The numerical results obtained after 14 days of column operation are
plotted also in the same figure. As seen in Fig. 2, the model simulates the biotransformation trend demonstrated by the experimental data. The deviations from the predicted values can be attributed to various factors such as variations of nutrients, primary substrates, and biomass along the column during the course of the experiment. Information on these variables is not available. Another possible reason for apparent discrepancies between predicted and measured concentrations is the deviation from the suggested biotransformation pathway due to other biotic and/or abiotic conversions.

Table 1 Model Parameters

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<tr>
<th></th>
<th>TCA</th>
<th>DCA</th>
<th>CA</th>
</tr>
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<tbody>
<tr>
<td>Maximum rate of substrate depletion (mole/l-day)</td>
<td>1.000</td>
<td>0.100</td>
<td>0.155</td>
</tr>
<tr>
<td>Half-saturation constant (mole/l)</td>
<td>0.0600</td>
<td>0.230</td>
<td>0.0075</td>
</tr>
<tr>
<td>Molecular weight with $^{14}$C atoms (g/mole)</td>
<td>137.5</td>
<td>103.0</td>
<td>68.5</td>
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<tr>
<td>Influent concentration (mg/l)</td>
<td>0.1</td>
<td>0</td>
<td>0</td>
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Fig. 2 Comparison of numerical results (solid lines) with experimental data (O TCA, □ DCA, △ CA) of Vogel and McCarty (1987) along an anaerobic fixed-film column after 14 days of operation.

The results of the effort presented in this paper could help us to evaluate various remedial schemes in addition to estimating the magnitude of initial contaminant. A mathematical analysis of in
situ biotransformation techniques utilizing this ability of soil microorganisms would greatly improve the efficiency of aquifer recovery operations. Furthermore, such an approach would help us to analyze the importance of individual mechanisms of the overall behavior of chlorinated hydrocarbons in soils and groundwater.

REFERENCES


