Report for 2004TX156B: Effect of Flow Velocity on Biodegradation of Trichloroethene (TCE) and Perchlorethene (PCE) During Restoration of Contaminated Groundwater Aquifers

- Other Publications:
  - Cunningham, J.A., and I. Mendoza-Sanchez, Equivalence of Two Models for Biodegradation During Contaminant Transport in Groundwater, submitted to Water Resources Research (Appendix).
  - Cunningham, J.A., and I. Mendoza-Sanchez (2004), On the Equivalence of Two Models for Biodegradation during Contaminant Transport in Groundwater, Eos Trans. AGU,85(47), Fall Meet. Suppl., Abstract H21E-1069 0800h (Appendix 1).
  - Mendoza-Sanchez I., (2005), Modeling the Effect of Mass Transfer on Contaminant Biodegradation in Groundwater, Texas Water 2005, Texas AWWA and WEAT, Student Presentation of Papers (Appendix 1).
- unclassified:
  - Mendoza-Sanchez I., (2005) Modeling the Effect of Groundwater Flow Velocity on Contaminant Biodegradation, Texas A&M University Water Week, Student Poster Competition (Appendix 1).

Report Follows

FINAL REPORT:
Effect of flow velocity on biodegradation of trichloroethene (TCE) and perchloroethene (PCE) during restoration of contaminated groundwater aquifers

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1. EXECUTIVE SUMMARY

Chlorinated ethenes (CE) are widespread contaminants in groundwater. Bioremediation of chlorinated ethenes is a viable low cost technique for decontamination of CE-contaminated sites. However, bioremediation is not fully controlled due to the lack of information of the phenomena involved. The purpose of this project is to improve our ability to predict and engineer the complete dechlorination of PCE and TCE to ethene in contaminated groundwater.

A mathematical model that accounts for the transport of the contaminants and the growth and detachment of the relevant bacteria has been developed. The mechanisms included in the mathematical model to characterize the contaminant biodegradation are: mass transport in the bulk liquid by advection and dispersion, mass transfer from the bulk liquid to the biofilm (BF) by diffusion, molecular diffusion within the BF, biological reaction within the BF, growth of the active bacteria, and shearing of the biofilm under the influence of groundwater flow. A simplified version of the mathematical model (which assumes the bacterial populations are at steady-state) has been solved numerically using a finite difference method with operator splitting and an iterative solution procedure.

The most important findings of the present study are: a) the numerical solution of the mathematical model is a practical approach to solve contaminant-reactive transport in porous media, b) preliminary results suggest that chemical mass transfer rate may be a limiting factor in the rate of biodegradation, b) chemical mass transfer depends on the flow velocity, therefore flow velocity may have a significant impact on the extent and/or rate of biodegradation of PCE. The next steps are: to implement the bacterial growth and detachment mechanisms in the model; to construct the lab-scale aquifer model; to design the operation of the experimental model based on the final results of the mathematical model; and to observe if the numerical simulation is able to predict experimental results.

2. INTRODUCTION

Trichloroethene (TCE) and perchloroethene (PCE, also known as tetrachloroethene) have been widely used as solvents and degreasing agents. Due to their wide use, their historic improper disposal, and their recalcitrance to degradation, TCE and PCE are widespread contaminants in groundwater. Because of their toxicity and suspected carcinogenicity, contamination of groundwater by TCE and PCE prevents the use of groundwater for drinking, irrigation, or nearly any other beneficial use. According to the U.S. Environmental Protection Agency (EPA) web site, there are, within the state of Texas, 26 sites on the National Priority List (also known as Superfund sites) at which the groundwater is contaminated. At most of these sites, the groundwater contaminants include chlorinated volatile organic compounds (VOCs), such as PCE, TCE, or other chlorinated solvents.

Biodegradation of PCE under anaerobic conditions is conducted by bacterially-mediated sequential reductive dechlorination [1]. That is, PCE is converted sequentially to TCE, dichloroethene (DCE), vinyl chloride (VC), and finally ethene, a benign end-product. Transformation of PCE to TCE and DCE is observed at almost all contaminated sites, but degradation of DCE to VC and ethene has been observed only at some sites. Consequently, DCE and VC often accumulate at contaminated sites. VC is the most toxic and carcinogenic of all the chlorinated ethenes.

Several factors have been identified that may affect the degree of dechlorination observed at contaminated sites. These factors include: the presence or absence of the dechlorinating bacterium *Dehalococcoides ethenogenes* [2–5]; the presence and activity of syntrophic fermentative bacteria to produce hydrogen for the dechlorinating species; a sufficient supply of electron-donating compounds [6–7]; competition among dechlorinating, sulfate-reducing, and methanogenic bacteria for nutrients and electron donors [8–9].

Finally, there is one factor that may be quite important with regard to the degree of dechlorination, but that has received relatively little attention so far: the flow velocity of the groundwater. Cabrirol et al. [10] observed that sulfate influenced the degree of dechlorination in batch reactors, but not in flow-through column reactors. This effect was attributed to two phenomena, namely, the rate of chemical mass transfer through the

active biofilm and the relative ability of different bacteria to adhere to the biofilm surface.

During the period of March 1, 2004 to February 28, 2005, the effect of flow velocity on biodegradation of perchloroethylene (PCE) and trichloroethylene (TCE) during restoration of contaminated groundwater aquifers was studied.

3. PROJECT GOALS

The objective of this research is to quantify the effect of groundwater flow velocity on the biodegradation of perchloroethene (PCE) and trichloroethene (TCE).

The hypothesis is that groundwater flow velocity may be one important factor with regard to the degree of dechlorination. Flow velocity may affect two important phenomena; the rate of chemical mass transfer through the active biofilm (BF), and the relative ability of different bacteria to adhere to the biofilm surface.

4. RESEARCH APPROACH

The work proposed in the original statement is to conduct experiments in sand columns to observe and analyze the effect of groundwater flow velocity on the biodegradation of PCE and TCE. In order to properly design the experiments and interpret the results, it is first necessary to develop a relatively sophisticated conceptual and mathematical model.

4.1. Conceptual Model

The framework of the mathematical model is that the rate of transformation of the contaminant will be a function of the flux of substrate from the bulk solution to the surface of the biofilm (see figure 1). The model will account for transport processes in the bulk solution, the mass transfer from the bulk solution to the biofilm, and diffusion and degradation inside the biofilm.

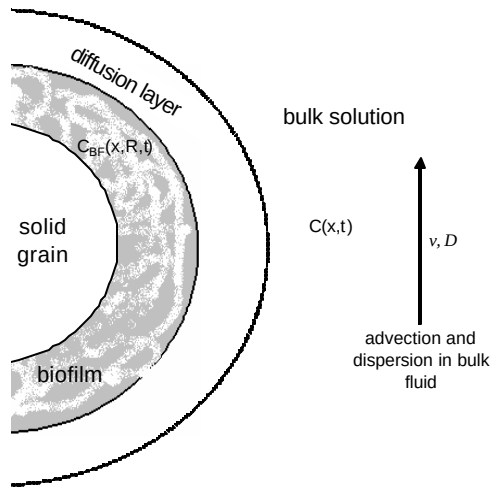


Figure 1. Schematic representation of the conceptual model

4.2. Mathematical Model

The equation used to describe the flux of substrate in the bulk solution is the advection-dispersion equation (ADE). Mass transfer is described adding a mass transfer term to the ADE equation resulting in an advection-dispersion-mass transfer equation (ADMTE) (1). Definition of the terms in the equation is given in table 1 at the end of this section.

$$\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} - v \frac{\partial C(x,t)}{\partial x} - \frac{3\ (1-n)}{n\ R_1}\ a\ \left[C(x,t) - C_{BF}(x, R = R_1, t)\right] \qquad (1)$$

Biodegradation is described inside the biofilm considering molecular diffusion and microbial transformation simultaneously. The microbial transformation is described using Monod Kinetics with a dual substrate limitation and competitive inhibition reaction (2). Hydrogen will be the limiting chemical substrate, and competition will exist between PCE, TCE, DCE, and VC for the available hydrogen to be used in the dechlorination process.

$$\frac{\partial C_{BF}(x,R,t)}{\partial t} = D_{BF}\frac{1}{R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial C_{BF}(x,R,t)}{\partial R}\right) - \frac{qXa(x,R,t)C_{BFi}(x,R,t)}{C_{BFi}(x,R,t)+K_i\left(1+\frac{C_{BFj}(x,R,t)}{K_j}\right)}\left(\frac{H(x,R,t)-H^*}{H(x,R,t)-H^*+K_h}\right) \quad \text{for } R_0 < R < R_1 \qquad (2)$$

The ADMT equation is coupled with the biofilm equation through the boundary condition in equation 3.

$$n_{BF}\ D_{BF}\ \frac{\partial C_{BF}(x,R=R_1,t)}{\partial R} = a\ \left[C(x,t) - C_{BF}(x,R=R_1,t)\right] \qquad (3)$$

The set of equations presented were solved for a hypothetical sand column with flow of PCE-contaminated water through the porous medium. For this case the boundary conditions, related to equation 1 are as follow: a) flux into the column equals flux just inside the column (4), and b) there is no dispersive flux at the end of the column (5).

$$v\frac{\partial C(x=0,t)}{\partial x} - D\frac{\partial C(x=0,t)}{\partial x} = vC^0 \qquad (4)$$

$$\frac{\partial C(x=L,t)}{\partial x} = 0 \qquad (5)$$

The boundary conditions for the biofilm equation (2) are the following. Mass flux to the surface of the biofilm ($R=R_1$) equals mass flux away from the surface of the biofilm (3). The boundary condition at the surface of the grain ($R=R_0$) is that there is no contaminant flux into the grain (6).

$$\frac{\partial C(x, R = R_0, t)}{\partial x} = 0 \tag{6}$$

No contaminant is present as an initial condition.

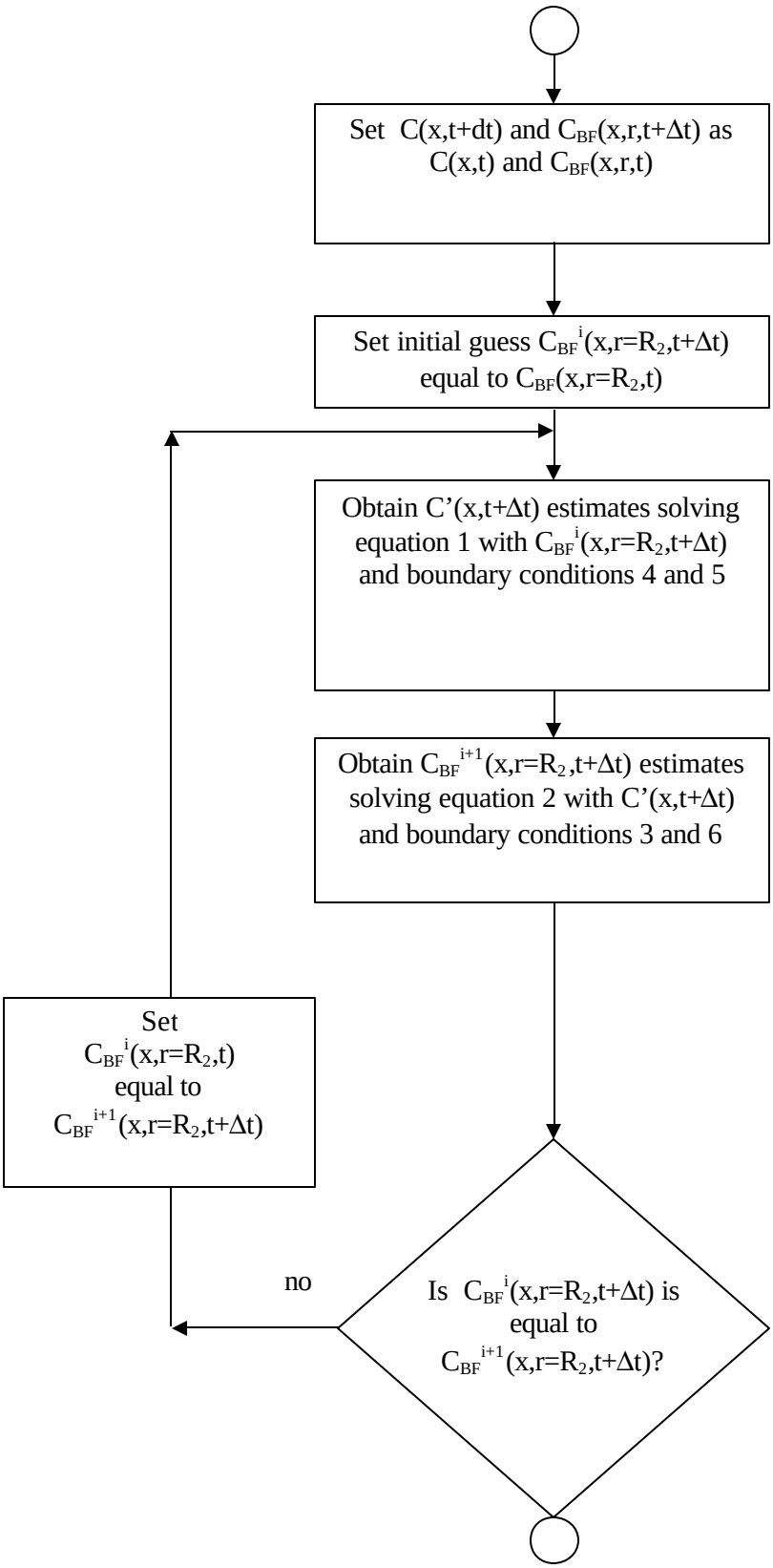
$$C(x, t = 0) = 0 \tag{7}$$

Table 1. Definition of the terms used in the equations.

Symbol	Definition	Dimensions
C	Concentration of the chemical in the bulk solution	ML^{-3}
v	Flow velocity of the groundwater	LT^{-1}
D	Dispersion coefficient	L^2T^{-1}
N	Porosity of the column	1
R0	Radius of the grain	T
R1	Radius of the grain + length of the biofilm thickness	L
α	Mass transfer coefficient from the bulk to the biofilm	LT^{-1}
C_{BF}	Concentration of the chemical inside the biofilm	ML^{-3}
C_{BFi} C_{BFj}	Concentration of the competitive chemicals inside the biofilm	ML^{-3}
Xa	Biomass concentration in the biofilm	ML^{-3}
n_{BF}	Porosity of the biofilm	1
D_{BF}	Diffusion coefficient within the biofilm	L^2T^{-1}
$\hat{q}$	Maximum specific dechlorination rate	$M_sM_x^{-1}T^{-1}$
K_i K_j	Half velocity coefficient for dechlorination	ML^{-3}
H	H2 concentration inside the biofilm	ML^{-3}
H*	Threshold concentration of H2 for dechlorination	ML-3
K_h	Half velocity coefficient for hydrogen consumption	ML^{-3}

4.3. Solution Procedure

The equations 1 and 2 are solved using initial and boundary conditions 3 to 7. Since the biofilm equation (2) is non-linear we solve the set of equations by splitting the ADMTE (1) and the biofilm equations (2), and coupling them by the boundary condition (3). The coupled equations have been solved using finite difference methods and Runge Kutta with operator splitting and an iterative solution procedure. We use the following procedure at each time step to solve the set of equations.


Set C(x,t+dt) and C_{BF}(x,r,t+Δt) as C(x,t) and C_{BF}(x,r,t)
Set initial guess C_{BF}^{i}(x,r=R_2,t+Δt) equal to C_{BF}(x,r=R_2,t)
Obtain C'(x,t+Δt) estimates solving equation 1 with C_{BF}^{i}(x,r=R_2,t+Δt) and boundary conditions 4 and 5
Obtain C_{BF}^{i+1}(x,r=R_2,t+Δt) estimates solving equation 2 with C'(x,t+Δt) and boundary conditions 3 and 6
Set C_{BF}^{i}(x,r=R_2,t) equal to C_{BF}^{i+1}(x,r=R_2,t+Δt)
no
Is C_{BF}^{i}(x,r=R_2,t+Δt) is equal to C_{BF}^{i+1}(x,r=R_2,t+Δt)?

This procedure allows us to use the best method to solve each operator. We split the system of equations in three operators: the advection-dispersion-mass-tranfer operator (1), the diffusion operator of the biofilm equation (2) and the reaction operator of the biofilm equation (2). Implicit finite difference method (Crank Nicolson) has been used to solve the ADMT and the biofilm diffusion operators, while fourth order Runge-Kutta was used to solve the biofilm reaction-operator.

Using the presented operator-splitting procedure it is possible to use different time steps for each operator, avoiding instabilities when using the Runge-Kutta numerical method. In addition different space steps and time steps may be used when instability problems occur when solving the implicit finite difference method. So the operator-splitting-iterative process helps us to save time and CPU operations compared to a whole system solution.

5. RESULTS

5.1. Modeling Results

Preliminary results for PCE reactive-transport along a cylindrical column with homogeneous grains were obtained (see figure 2). Further development of the numerical modeling is necessary to obtain values of concentration of PCE, TCE, cis-DCE, VC, ethene, hydrogen, and biomass density in space and time. Results from the mathematical model will be used to design the chemical and biological analysis necessary in the experimental phase of the project.

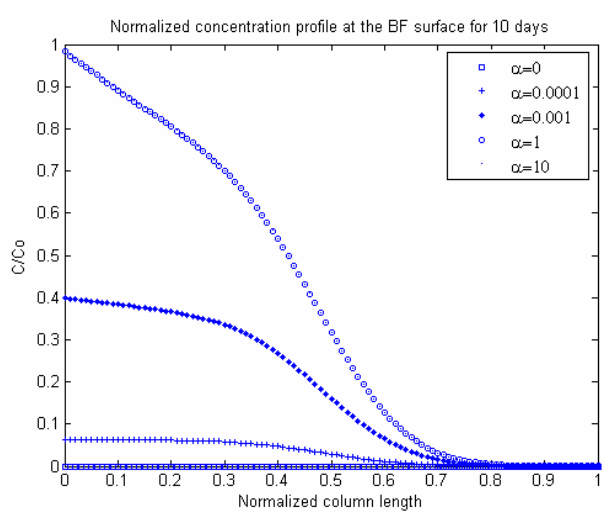


Figure 2: Concentration at the surface of the biofilm mass transfer coefficient (a) units is cm/day

6. RECOMMENDATIONS FOR FUTURE WORK

6.1 Laboratory Experiments

The design of the soil columns as lab-scale models of contaminated aquifer has been completed. Columns consist of acetal delrin hollow rods with 0.05 m (2 inch) inside diameter, 0.06 m (2.5 inch) outside diameter, and 0.76 m (30 inch) length. This material was chosen due to its resistance to chlorinated ethenes. The hollow rods (tubing) will be sealed at the top and bottom with two 0.08 m (3 inch) diameter discs of the same material. The discs, top end, and bottom end of the tubing will be threaded and tap so the discs could be screwed and sealed to the tubing. Both discs will be drilled to allow a 0.015 m (5/8 inch) to 0.06 m (1/4 inch) stainless steel reduction union to provide inlet and outlet of water coming through the column. A stainless steel screen will be placed in the interior of each disc to prevent solid particles from exiting with the flow of water. The columns were designed to have sampling ports located at every 0.20 m along the column. The sampling ports were constructed by drilling the columns to allow 0.06 m (1/4 inch) stainless steel unions (1/4 inch NPT to 1/4 inch Swagelok). Sampling ports are equipped with 0.008 m (10/32 inch) Thermogreen GC septa in order to avoid introduction of oxygen each sampling time. Twelve identical columns will be constructed. Figure 3 shows a diagram of the column design.

Columns will be wet-packed with well-graded 0.002 m mean diameter sand. Before packing each column will be sterilized. Approximately 0.05 m section of the top and bottom of the column will be filled with 0.002 m mean diameter glass beads. Each column will be filled half full with de-ionized water. Saturated sand will be poured into the column and allowed to settle. Discs will be screwed and sealed to the top of the column. After packing each column will be placed in horizontal position.

Water flow rates through the columns were designed to span the range of realistic groundwater flow velocities. Thus columns will be fed at the following velocities: 0.01, 0.03, 0.05, 0.07, 0.09, and 0.12 m/day. So we will obtain a travel time range from 6 to 76 days. Each column will receive water at a constant rate by means of a peristaltic pump consisted of a Masterflex ® L/S® variable speed economy drive, 3 L/S® 4-Channel, 8

roller pump heads equipped with Masterflex ® L/S® small cartridges. Each pump channel with a defined velocity will be connected to each column. Twelve columns will operate at six different flow rates so two columns will have the same hydraulic conditions in order to replicate the tests.

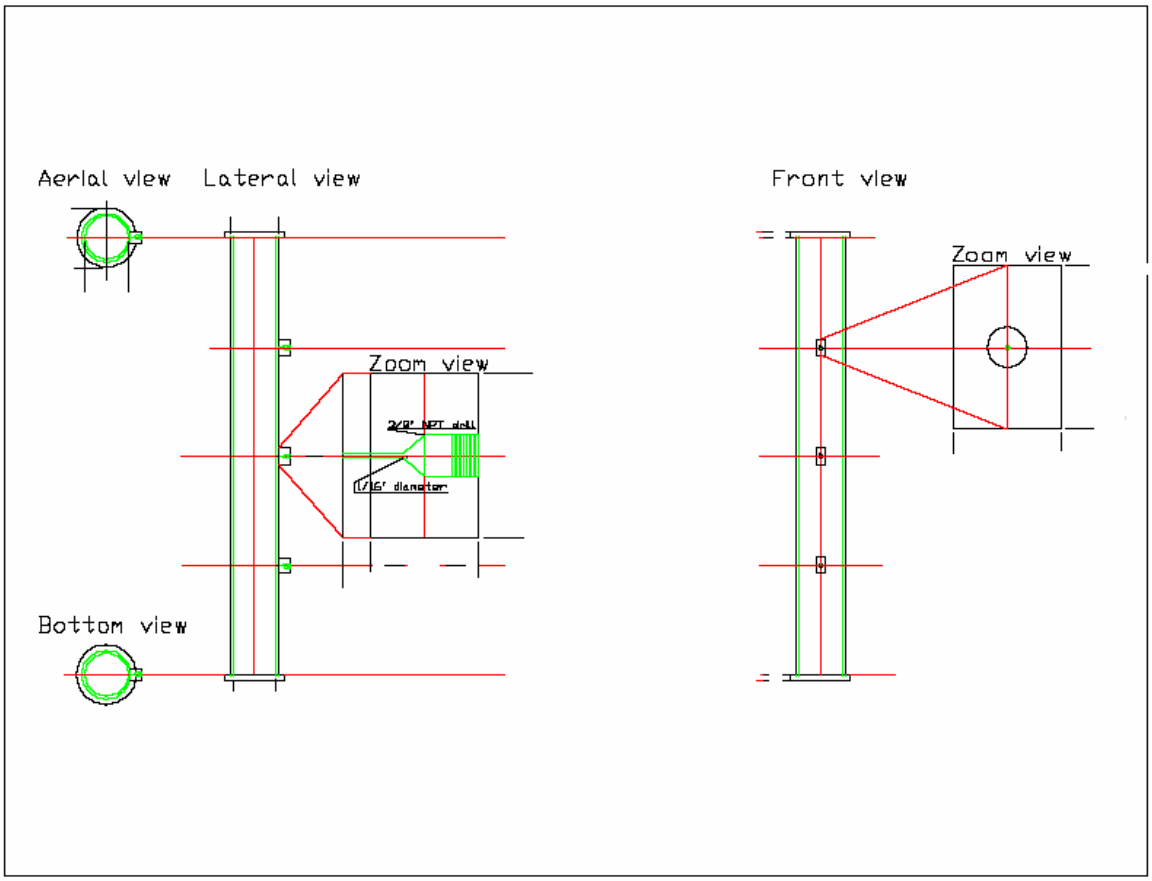


Figure 3. Column design

Contaminated water of known chemical composition will be pumped through the column continuously until equilibration. Then biodegradation will be initiated by inoculating the columns with a culture that is known to degrade PCE completely to ethene

Samples will be taken at regular intervals from the columns' sample ports. We will define the sampling size and intervals from the preliminary mathematical model results. It is likely that at early times more frequent intervals will be required, while at later times more spaced intervals will suffice. Samples will be taken by means of gas

tight syringes and will be analyzed for the concentration of chlorinated ethenes, ethene, hydrogen, and biomass concentration.

Analysis of chlorinated ethenes, ethene, and hydrogen will be performed by means of gas chromatographs equipped with flame ionization detector, thermal conductivity detector, and reduction gas detector.

Change in culture composition along space and time will be obtained in order to correlate velocity with community structure. Biomass concentration will be estimated by volatile suspended solids analysis of the samples. Analysis for biological community structure this will be accomplished by using appropriate molecular biological tools (DGCE, T-RFLP, PCR).

6.2. Additional Mathematical Modeling

Follow-up work to the mathematical and experimental modeling is to conduct a sensitivity analysis of the mathematical model. These results will allow us to determine how the dechlorination rate of TCE and PCE depends upon the groundwater flow velocity.

7. SUMMARY AND CONCLUSIONS

The mathematical model developed in this project represents a first step to improve our ability to predict and engineer complete dechlorination of PCE and TCE to ethene in contaminated groundwater.

To date, the effect of flow velocity on the extent of biodegradation of chlorinated ethenes has been only mildly explored or quantified. This project is significant because it will model the degradation potential of dechlorinating consortia based on flow velocity, chemical transport, and microbial transport in a contaminated aquifer. This, in turn, will allow us to advance the field of bioremediation. For instance, new tools or strategies that might result from this project include: determination if a particular contaminated site would be amenable to remediation by natural attenuation; optimization of the design of engineered remediation strategies that involved forced gradients (i.e., injection or extraction wells); and/or a method for determining the optimal location and rate of microorganism addition during bioaugmentation.

8. REFERENCES

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