Numerical Simulation of the Anaerobic Transformation of Tetrachloroethene (PCE) to Ethene in a Continuous Flow Aquifer Column

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ABSTRACT

Numerical modeling was conducted to simulate reactive transport with sequential anaerobic transformation processes in continuous-flow columns and compared with experimental observations. The column studies were conducted with continuous flow and injection of PCE in synthetic groundwater. The column was packed with aquifer solids from the Hanford DOE site and bioaugmented with the Evanite (EV) dechlorinating enrichment culture. In the first continuous flow column experiment, enhanced desorption resulting from anaerobic reductive dechlorination of PCE was simulated and compared with experimental observations (Figure 1). The experiments showed that cis-dichlorethene (c-DCE) concentrations in the column effluent exceeded the influent PCE concentration. In the second continuous-flow column experiment pre-reduced soil was used and a rapid reduction of PCE to ethene was observed. Simulating the second column using two microbial communities captured the observed CAHs breakthrough curves. Comparing model predictions with dehalogenation observations, reasonable agreement for CAHs transformation processes were found when using kinetics, inhibition constants and sorption parameters which were determined in batch laboratory experiments.

OBJECTIVES

- Simulate reactive transport in continuous-flow column based on experimentally determined kinetics, inhibition constants and sorption parameters.
- Model rate-limited enhanced desorption and biological transformation processes during one dimensional solute transport.
- Develop a model for complete PCE reductive dechlorination to ethene in continuous flow column that incorporates inhibition between chlorinated ethenes and rate-limited sorption desorption.
- Develop a model with two microbial dehalogenating systems and simulate the biotransformation based on the spatial distribution and activity of the biomass.

METHOD and APPROACH

Batch sorption experiments

Batch experiments were performed to independently determine the solid:liquid distribution coefficient (K_d) of PCE and its transformation products, and the first order mass transfer coefficient (K) between the aqueous and solid phase. All batch experiments were carried out in triplicate in 156 mL glass reactors. The reactors were filled with an approximately 1:1 solid liquid (w/w) ratio. Stock solutions containing the CAHs were spiked into each reactor. The following equations were used to model time dependent batch sorption experiments:

$$\frac{\partial C_{PCE}}{\partial t} = \frac{-Vs}{VL} * \frac{\rho}{\theta} * K * (K_d * C - S) \qquad (1)$$

$$\frac{\partial S_{PCE}}{\partial t} = K * (K_d * C - S) \qquad (2)$$

Column Experiment 1: Continuous-flow anaerobic column experiment was performed using Hanford soil bioaugmented with EV culture, the column was fed lactate as a fermenting electron donor. The column is 30 cm long and 7 cm diameter.

Column Experiment 2: Using the same aquifer material and culture, the effect of the pre- reduction of aquifer material was evaluated. The aquifer material was pre-treated with 5 mM Na_2S solution to reduce Fe (III) to Fe (II).

	soil water partitioning coefficient K_d (L/K_g)	mass transfer coefficient K (1/day)
PCE	1.9	0.068
TCE	0.76	0.032
cDCE	0.23	0.021
VC	0.099	0.009
Eth	0.031	0.005

Table 1: Sorption Kinetic parameter values determined for Hanford soil and CAHs using batch experiments.

	k_{max} (μmol/mg of protein/day)	K_S (μmol/L)
PCE*	12.4	1.63
TCE*	125	1.8
c-DCE$	13.8	1.76
VC $	8.08	62.6
Y	0.006	
K_d (d^{-1})	0.024	

Table 2: Kinetic parameter values determined for the Evanite cultures. * Yu and Semprini, (2004), $ used for 2nd dehalogenating population.

$$\frac{\partial C_{TCE}}{\partial t} = D\frac{\partial^2 C_{TCE}}{\partial x^2} - v\frac{\partial C_{TCE}}{\partial x} + \frac{K_{max,PCE} X * C_{PCE}}{K_{S,PCE} + C_{PCE}} - \frac{-K_{max,TCE} X * C_{TCE}}{K_{S,TCE}\left(1+\frac{C_{PCE}}{K_{CI,PCE}}\right) + C_{TCE}\left(1+\frac{C_{TCE}}{K_{HI,TCE}}\right)}$$

$$-\frac{\rho_b}{\theta}[K_{TCE}(K_{d,TCE} * C_{TCE} - S_{TCE})] \qquad (5)$$

$$\frac{\partial S_{TCE}}{\partial t} = K_{TCE}(K_{d,TCE} * C_{TCE} - S_{TCE}) \qquad (6)$$

$$\frac{\partial C_{cis-DCE}}{\partial t} = D\frac{\partial^2 C_{cis-DCE}}{\partial x^2} - v\frac{\partial C_{cis-DCE}}{\partial x} + \frac{K_{max,TCE} X * C_{TCE}}{K_{S,TCE}\left(1+\frac{C_{PCE}}{K_{CI,PCE}}\right) + C_{TCE}\left(1+\frac{C_{TCE}}{K_{HI,TCE}}\right)}$$

$$-\frac{\rho_b}{\theta}[K_c(K_{d3} * C_{cis-DCE} - S_{cis-DCE})] \qquad (7)$$

$$\frac{\partial S_{cis-DCE}}{\partial t} = K_c(K_{d3} * C_{cis-DCE} - S_{cis-DCE}) \qquad (8)$$

$$\frac{\partial X}{\partial t} = y\left[\left(\frac{K_{max,PCE} * X * C_{PCE}}{K_{S,PCE} + C_{PCE}} + \frac{K_{max,TCE} X * C_{TCE}}{K_{S,TCE}\left(1+\frac{C_{PCE}}{K_{CI,PCE}}\right) + C_{TCE}\left(1+\frac{C_{TCE}}{K_{HI,TCE}}\right)}\right.\right.$$

$$+\frac{K_{max,cis-DCE} X * C_{cis-DCE}}{K_{S,cis-DCE}\left(1+\frac{C_{TCE}}{K_{CI,TCE}}\right) + C_{cis-DCE}\left(1+\frac{C_{cis-DCE}}{K_{HI,cis-DCE}}\right)}$$

$$\left.\left.+\frac{K_{max,VC} X * C_{VC}}{K_{S,VC}\left(1+\frac{C_{TCE}}{K_{CI,TCE}}+\frac{C_{cis-DCE}}{K_{CI,cis-DCE}}\right) + C_{VC}\left(1+\frac{C_{VC}}{K_{HI,cis-DCE}}\right)}\right)\right] - K_d * X \qquad (9)$$

Where:
C: aqueous concentration, S: sorbed concentration, D: dispersion coefficient , V: velocity, K_{max}: the maximum specific utilization rate, X: the total biomass, K_s: the half-saturation coefficient, ρ : soil bulk density, θ: porosity, Vs: soil volume, VL : liquid volume , K_{CI} : Competitive inhibition constant.

The resulting sets of simultaneous equations were numerically solved by the finite element technique (COMSOL 3.3).

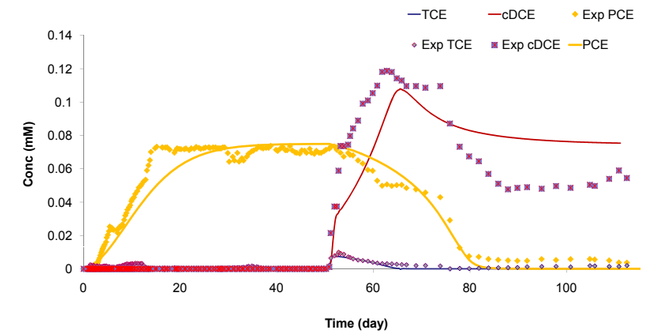

Figure 1: Simulation and experimental results of CAHs effluent concentration in continuous-flow column (Column experiment 1)

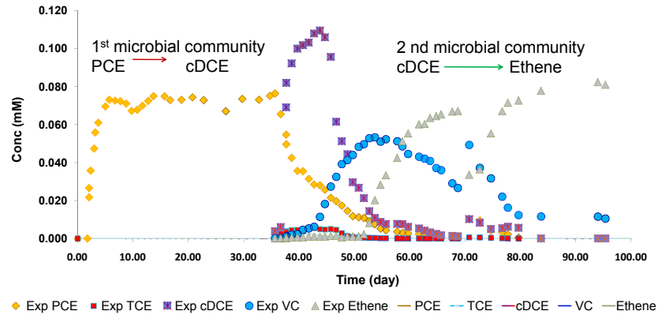

Figure 2: Simulation and experimental results of CAHs effluent concentration after 6 cm in continuous flow column, using pre- reduced aquifer material (Column experiment 2) .

MODEL DEVELOPMENT

An advection and dispersion transport was coupled with rate-limited desorption and reductive dechlorination (including competitive inhibition and microbial growth and decay) to describe the fate and transport processes occurring in continuous flow system fed PCE. The kinetics for the EV culture (Table-2) used in the model simulations were those determined by Yu & Semprini (2004). Sorption parameters (K_d and K) were determined by least square fit of the model equations (Eqn1 & 2) to batch experimental results (Table-1). Competitive inhibition constants (K_{CI}) were set equal to their respective half-velocity coefficients (K_s) (Yu, 2004). Initial biomass distribution was assumed to be in the first 5 cm of the influent part of the columns.
Equations 3-9 were used for the simulation shown in Figure-1. The same equations were used for the simulation shown in Figure-2 by adding cDCE transformation to Eqn-7 and with similar additional equations for VC transformation and ethene production.

$$\frac{\partial C_{PCE}}{\partial t} = D\frac{\partial^2 C_{PCE}}{\partial x^2} - v\frac{\partial C_{PCE}}{\partial x} - \frac{K_{max,PCE} X * C_{PCE}}{K_{S,PCE} + C_{PCE}}$$

$$-\frac{\rho_b}{\theta}[K_{PCE}(K_{d,PCE} * C_{PCE} - S_{PCE})] \qquad (3)$$

$$\frac{\partial S_{PCE}}{\partial t} = K_{d,PCE}(K_{PCE} * C_{PCE} - S_{PCE}) \qquad (4)$$

DISCUSSION

- Model simulations show higher c-DCE concentrations in the effluent compared to influent PCE concentration, consistent with the experimental results indicating enhanced desorption of PCE from the aquifer material.
- Simulating columns 1 and 2 with biomass distributed spatially in the column influent where they were bioaugmented gives good agreement with the experimental results. The results indicated that most of the transformations occur near the influent part of the column.
- Successful simulation of the second column using two dehalogenating communities supports the hypothesis that at least two populations are responsible (Figure 2).
- Biodegradation rates of CAHs during flow in porous media often depends on the mixing between nutrients and CAHs . Experimental results from port one (Figure-2) shows tailing in breakthrough curves which may be due to insufficient mixing between nutrients and CAHs that are flowing through the aquifer material.

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CONCLUSIONS

- **The simulations indicated that enhanced desorption responsible for the increase in effluent cDCE concentration above the influent PCE.**
- **The simulations indicated that two dehalogenating communities are likely responsible for the transformation of PCE to ethene.**
- **Simulation of continuous-flow column using batch laboratory generated microbial and sorption kinetics captured the overall response observed in the column experiments.**
- **Insufficient mixing at the column influent likely resulted in deviations from 1-D transport and the tailing observed in Figure 2.**
- **Future work will continue to evaluate electron donor limitations and competition for electron donor in continuous-flow column and incorporating two microbial population in the modeling analysis.**

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