한국지하수토양환경학회 추계학술발표회
2004년 9월 9~10일 전 주 대 학 교

# Haldane Inhibition at CAH DNAPL Source Zone in Soil and Groundwater

**Seungho Yu**, Lewis Semprini

*Dept of Civil, Construction, and Environmental Engineering Oregon State University (yuse@engr.orst.edu)*

ABSTRACT

Two biokinetic models (① Michaelis-Menten kinetics with competitive inhibition ② with both competitive inhibition and Haldane inhibition) for reductive dechlorination were developed and compared with results from batch kinetic tests conducted over a wide range of PCE and TCE concentrations with two different dechlorinating cultures. At PCE concentrations lower than 300 $\mu$M, both model simulated the experimental results well. However, The kinetic model that incorporated both competitive and Haldane inhibitions much better simulated experimental data for PCE concentrations greater than 300-400 $\mu$M, and TCE concentrations at half its solubility limit (4000 $\mu$M). The PM culture showed Haldane inhibition constants of 900, 6000, 7000 $\mu$M for TCE, c-DCE and VC, indicating very weak Haldane inhibition for c-DCE and VC, while the EV culture had lower Haldane inhibition constants for TCE, c-DCE, and VC of 900, 750, and 750 $\mu$M, respectively. The BM culture had better transformation abilities than the individual cultures over a wide range of PCE and TCE concentrations. Modeling results indicated that a combination of competitive and Haldane inhibition kinetics is required to simulate dechlorination over a broad range of concentrations up to the solubility limits of PCE and TCE.

Key word: reductive dechlorination, PCE, TCE, competitive inhibition, Haldane inhibition.

## 1. INTRODUCTION

Anaerobic reductive dechlorination is an important process for the bioremediation of the contaminated subsurface, especially for the detoxification of highly chlorinated compounds, such PCE and TCE, that can be present at high concentrations due to the presence of dense non-aqueous phase liquid (DNAPL) (Rittmann et al., 1994). The previously developed models for reductive dechlorination of CAHs did not consider inhibition effects between all chlorinated ethylenes (Fennell and Gossett, 1998; Cupples et al., 2004). Furthermore, the models were used to fit the experiment data with PCE or TCE concentration lower than 300 $\mu$M.

Recently, we experimentally determined maximum degradation rates ($k_{max}$) and half-velocity coeffi-

cients ($K_S$) for each step of the dechlorination of PCE to ETH for two different mixed cultures and evaluated inhibition between chlorinated ethylenes (Yu et al., 2004). The study presented here aims to simulate the sequential transformation of PCE and TCE to ETH over a broad range of concentrations up to the solubility limitof PCE and half the solubility limit of TCE in water. The kinetic models developed for each culture were also combined to simulate the transformation ability of a binary mixed culture composed of each dechlorinating culture.

## 2. METHODS AND MODEL DEVELOPMENT

**Dechlorinating Cultures.** The two anaerobic mixed cultures used in this study were isolated from Point Mugu Naval Weapon Facility, California (PM) and the Evanite site in Corvallis, Oregon (EV). The third culture used was a binary mixed culture (BM), representing a mixture of the PM and EV cultures (1:1 volume ratio). PCR assay targeting genes encoding for 16S ribosomal RNA indicated that the PM and EV cultures had Dehalococcoides-like microorganisms present with the ability of complete reductive dechlorination to ETH (Yu and Semprini, 2004; Yu et al., 2004).

Table I. Experimental conditions of kinetic batch reactors

| Run | PM | | EV | | BM | | |
|---|---|---|---|---|---|---|---|
| | Initial CAH ($\mu$M) | Measured Cell Concentration (mg-protein/L) | Initial CAH ($\mu$M) | Measured Cell Concentration (mg-protein/L) | Initial CAH ($\mu$M) | Measured Cell Concentration (mg-protein/L) | Relative Proportions of Each Cultures (PM:EV) (mg-protein/L) |
| 1 | 92[a] | 25 | 39[a] | 30 | 43[a] | 28 | 13:15 |
| 2 | 282[a] | 34 | 282[a] | 30 | 317[a] | 31 | 14:17 |
| 3 | 1128[a] | 34 | 1057[a] | 27 | 1128[a] | 30 | 14:16 |
| 4 | 3875[b] | 35 | 4173[b] | 40 | 4173[b] | 37 | 17:20 |

[a]PCE, [b]TCE

**Model Development.** The kinetic equations for reductive dechlorination by the mixed cultures are presented as Equation 1 with both competitive and Haldane inhibition included. In contrast to competitive inhibition, where one CAH inhibits the transformation of another CAH, with Haldane inhibition the CAH inhibits its own transformation.

$$\frac{dC_y}{dt} = \frac{-k_{\max,y} X C_y}{K_{S,y}\left(1+\frac{C_x}{K_{CI,x}}\right)+C_y\left(1+\frac{C_y}{K_{HI,y}}\right)} \qquad \text{(Equation 1)}$$

Our previous studies with two anaerobic mixed cultures (PM and EV) indicated inhibition was competitive and the more chlorinated ethylenes inhibited reductive dechlorination of the less chlorinated ethylenes with inhibition constants equal to the KS values (Yu and Semprini, 2004). However, the less chlorinated ethylenes very weaklyinhibited the more chlorinated ethylenes.

## 3. RESULTS

**Reductive Dechlorination of PCE by the PM, EV, and BM Cultures.** For the PM culture, both

models yield similar results. The $K_{HI}$ values for TCE, c-DCE, and VC were obtained from heuristic fits of both PCE and TCE dechlorination data. The results show that both models simulate very well the temporal histories of chlorinated ethylenes, as well as the response to changes in initial PCE concentrations.

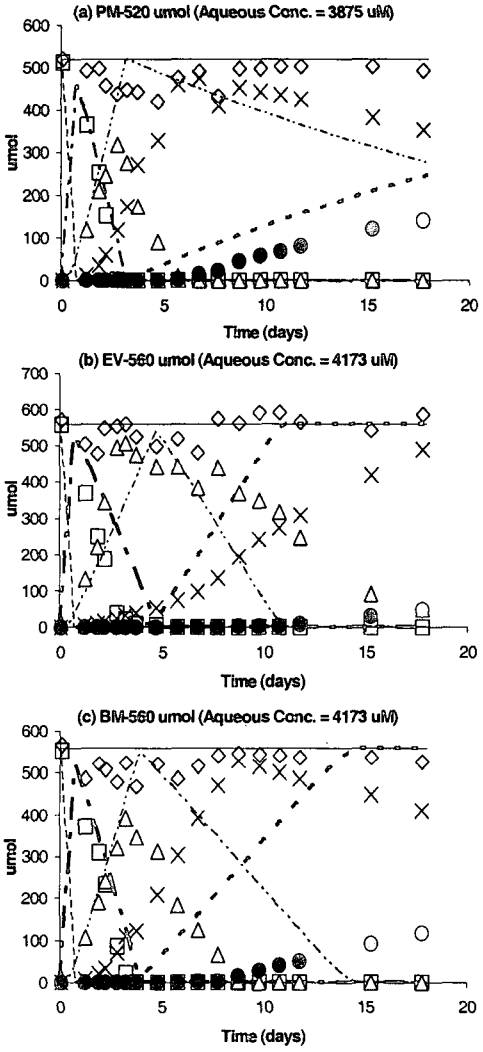


Figure 1. Reductive dechlorination kinetics at high TCE concentrations by the PM, EV and BM cultures. The lines represent model simulations with competitive inhibition kinetics.

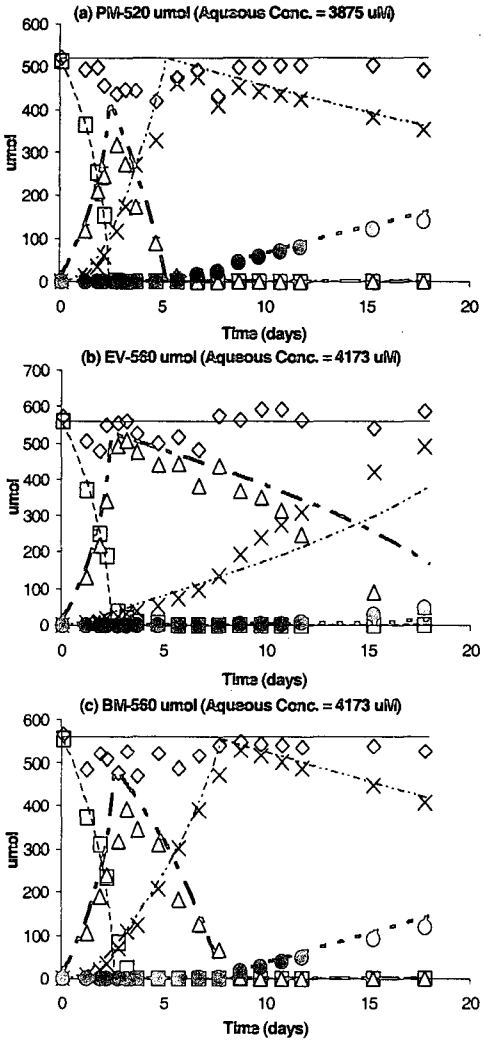


Figure 2. Reductive dechlorination kinetics at high TCE concentrations by the PM, EV and BM cultures. The lines represent model simulations with Haldane and competitive inhibition kinetics

For the EV culture, the simulations with competitive inhibition model fit the experimental data reasonably well for initial PCE concentrations of 39 and 282 $\mu$M. At the highest PCE concentration of 1057 $\mu$M, however, the model did not simulate sequential PCE dechlorination as well. The simulations including both competitive and Haldane inhibition kinetics fit the experimental data better than those only with competitive inhibition.

For the BM culture, both models showed similar sequential transformation at the lowest PCE concentration (43 $\mu$M). At the higher PCE concentrations of 317 and 1128 $\mu$M, the model with competitive and Haldane inhibition kinetics provided a better fit to the experimental data than the model with only competitive inhibition kinetics.

**Reductive Dechlorination of a High TCE Concentration.** Simulations using only competitive inhibition and both competitive and Haldane inhibition are shown in Figures 1 and 2, respectively. Using only competitive inhibition kinetics, the dechlorination of TCE to ETH by all three cultures was predicted to occur more rapidly than was actually observed (Figure 1). Model simulations with both competitive and Haldane inhibitions (Figure 2) simulated the experimental data much better.

## 4. CONCLUSION

The PM culture has very high Haldane inhibition constants for c-DCE and VC (6000 and 7000 $\mu$M, respectively), indicating very weak Haldane inhibition effects. The EV culture, however, showed significant Haldane inhibition for TCE, c-DCE, and VC. Both competitive and Haldane kinetics were required to model the experimental observations for the anaerobic reductive dechlorination of CAHs at high concentrations, possibly produced from DNAPL source zone.

With a broad range of PCE and TCE concentrations, the BM culture obtained transformation abilities of both cultures. The BM culture showed overall good performance when both PCE and TCE test results were considered. Bioaugmentation with a binary mixed culture might be more effective at real contaminated sites, where wide ranges in concentrations and contaminant mixture are present.

## 5. REFERENCES


(1) Cupples AM, Spormann AM, McCarty PL. 2004. Vinyl chloride and cis-dichloroethene dechlorination kinetics and microorganism growth under substrate limiting conditions. Environ Sci Technol 38: 1102-1107.

(2) Fennell DE, Gossett JM. 1998. Modeling the production of and competition for hydrogen in a dechlorinating Culture. Environ Sci Technol 32: 2450-2460.

(3) Rittmann BE, Seagren E, Wrenn BA. 1994. In: In-situ bioremediation. Second Edition. Parkridge. New Jersey: Noyes Publications. p 37-50.

(4) Yu S, Semprini L. 2004. Kinetics and modeling of reductive dechlorination at high PCE and TCE concentrations. Biotech and Bioeng. (In Press).

(5) Yu S, Dolan ME, Semprini L. 2004. Kinetics and inhibition of reductive dechlorination of chlorinated ethylenes by two different mixed cultures. Environ Sci Technol (In Press).