Modelling and probabilistic risk analysis of enhanced anaerobic bioremediation of chlorinated ethenes

C. A. SHOEMAKER, M. WILLIS & I. BENEKOS
School of Civil & Environmental Engineering, Cornell University, Ithaca, New York 14853, USA
cas12@cornell.edu

Abstract This paper gives an overview of modelling, sensitivity analysis and probabilistic risk assessment of bioremediation of a contaminant and its three daughter products, which are also toxic. The analysis is applied to chlorinated ethenes, an important class of groundwater contaminants. Chlorinated ethenes, including tetrachloroethene (PCE), and its daughter products trichloroethene (TCE), dichloroethene (DCEs) and vinyl chloride (VC), can be biologically degraded under anaerobic conditions. Injection of organic compounds (donors) that ferment to provide hydrogen can enhance the activity and growth of dechlorinating microorganisms that degrade chloroethenes. This analysis is a tool that is valuable in understanding and designing enhanced anaerobic bioremediation of chlorinated ethenes.

Key words bioremediation; chlorinated ethenes; groundwater; PCE; probabilistic risk assessment; risk; TCE

INTRODUCTION AND BACKGROUND INFORMATION

An important class of groundwater contaminants consists of chloroethenes—tetrachloroethene (PCE) and its daughter products: trichloroethene (TCE), dichloroethene (DCE) and vinyl chloride (VC). All these chemicals are toxic, especially vinyl chloride. Direct extraction pumping (e.g. "pump and treat") for these contaminants can be very expensive and in some cases ineffective.

However, these materials can be remediated in situ by anaerobic biodegradation to non-toxic ethene. Injection into the groundwater of organic compounds (donors) that ferment to provide hydrogen can enhance the activity and growth of dechlorinating microorganisms that degrade chloroethenes. Figure 1 shows the four steps involved in transforming PCE to ethene. Each step is accelerated in the presence of adequate hydrogen and adequate concentrations of dechlorinator bacteria.

Design of enhanced bioremediation of chlorinated ethenes requires decisions about the location of wells, the rates of injected water and donor, and the rates of extracted or recirculated water. Although bioremediation can be faster and less expensive than pump and treat methods for these problems, it is nevertheless expensive. Hence, a model can be very useful to help design cost-effective treatment systems as well as to help gain further understanding of the scientific processes important in reductive dechlorination.
MODELLED SYSTEM

There are a number of microbiological populations that are required for degradation of the chlorinated ethenes and associated by-products. The kinetic reactions described by Fennell & Gossett (1998) are complex. They require nine chemical species and four biological species to transform them. Let *italics* denote the microbiological populations. *Donor fermenters* are needed to transform the donor butyrate into $\text{H}_2$ and acetate. *Acetotrophic methanogens* are required to transform acetate into $\text{CH}_4$. *Dechlorinators* transform PCE + $\text{H}_2$ into TCE (and perform additional dechlorination steps). *Hydrogenotrophic methanogens* utilize $\text{H}_2$ to produce $\text{CH}_4$. Since *dechlorinators* require hydrogen (which is limited) to degrade chlorinated ethenes, they must compete with *hydrogenotrophic methanogens*, which also consume hydrogen.

As indicated in Fig. 1, it is important that hydrogen and dechlorinator bacteria be available at each location where contamination exists. Since the contaminants and the donor will move during the remediation period, it is essential that a transport model be developed which incorporates the reactions of all the elements in Fig. 1.

Willis (2000) has developed a fate-and-transport model CORDITE for halogenated-organic contaminants that properly incorporates hydrogen dynamics and competition by building upon the batch model (e.g. a model without transport) developed and verified with laboratory data by Fennell & Gossett (1998 and Fennell et al., 1997). All of the chemical and biological species in Fig. 1 are included in the CORDITE model. The model tracks the fate and transport of a total of 13 chemical and biological species including PCE, TCE, DCE, vinyl chloride, ethene, a hydrogen donor (e.g. butyrate), dechlorinator bacteria, and methanogenic bacteria. The two types of bacteria compete for hydrogen.

The CORDITE equations developed by Willis & Shoemaker are incorporated into a module for the reactive transport code RT3D (Clement et al., 1998) and the transport code MT3D (Zheng & Wang, 1998). The equations for spatially distributed microbial growth dynamics involve Monod growth equations, which are highly nonlinear.
TRANSPORT EQUATIONS

The transport equations for the 13 species of interest are given by:

\[
\frac{\partial C_\omega}{\partial t} = \frac{\partial}{\partial x_i} \left( D_i \frac{\partial C_\omega}{\partial x_i} \right) - \frac{\partial}{\partial x_i} \left( v_i C_\omega \right) + \frac{q_{\omega}}{\Theta} C_\omega^{ini} + \frac{1}{R_\omega} r_\omega
\]

where \( C_\omega \) is the concentration of species \( \omega \) dissolved in groundwater, \([\text{M L}^{-3}] \) (\( \omega = 1, 13 \) for PCE, TCE, DCE, VC, etc.), \( C_\omega^{ini} \) represents injected mixture concentration of species \( \omega \) \([\text{M L}^{-3}] \), \( R_\omega \) is the retardation factor of contaminant \( \omega \), and \( r_\omega \) represents reactions of the contaminant.

The remaining terms in the equation above are commonly used and are not defined here to save space. The retardation coefficient \( R_\omega \) is quite different among the four chlorinated ethenes, with PCE being the least mobile and VC being the most mobile compound. The terms \( r_\omega \) in the equation above are highly nonlinear functions of the concentrations \( C_\omega \) incorporating Monod growth kinetics in the non-transport model by Fennell & Gossett (1998). The transport equations and the specific form of the \( r_\omega \) terms are described in Willis (2000).

DECHLOR: USER-FRIENDLY SOFTWARE

SERDP/ESTCP in US Department of Defense (US-DOD) is funding the development of a user-friendly version DECHLOR, a chlorinated ethenes model that has an expansion of the equations for CORDITE given above. DECHLOR is an expansion of CORDITE since it has 18 species to incorporate more types of donors (Shoemaker et al., 2001b). A user-friendly graphical user interface is currently being developed, the FORTRAN module and graphical user interface for DECHLOR, which will be distributed at little or no cost when development is complete.

APPLICATION OF DECHLOR TO FIELD DATA

As evidence of the importance of this method (injection of a hydrogen donor) for remediation of chlorinated ethenes, the US Department of Defense's SERDP/ESTCP program has applied the RABITT (Reductive Anaerobic Biological In-Situ Treatment Technology) protocol to four US DOD field sites throughout the US. Professor Gossett has also been collecting microcosm data for each of these sites.

Shoemaker et al. (2001a) have applied DECHLOR to RABITT field data from Cape Canaveral. The field data collection was supervised by Alleman et al. (2000). At this site there were two recirculating wells, one which injected donor at the top of the recirculation area and one of which injected donor at the bottom. This was modelled by a three-dimensional (3-D) version of DECHLOR. The preliminary results for TCE and DCE at this site were excellent. Remarkably, the biokinetic parameter values did not need to be changed from those originally used by Fennell & Gossett in their original batch model based on laboratory data. Additional modelling work on boundary...
conditions is required for vinyl chloride, which is more mobile that the other chlorinated ethenes. Simulation results for TCE at Cape Canaveral are shown in Fig. 2.

**SENSITIVITY AND OPTIMIZATION ANALYSIS**

Willis (2000) did an extensive sensitivity analysis of the CORDITE model predictions as a function of changes in parameter values. He found that the most sensitive parameter by far was soil temperature. He also found that the responses were nonlinear and not symmetric, hence the rate of change (i.e. the sensitivity) is not constant. Using the temperature used in the laboratory studies for the base case, he found that PCE retardation and the half velocity constant for the reaction between hydrogen and dechlorinator bacteria were also very sensitive parameters.

Willis (2000) also applied the evolutionary algorithm DES (derandomized evolution strategy) and a genetic algorithm to the problem of finding the best location of wells and injection strategies. He used DES because Yoon & Shoemaker (1999) found this to be the best evolutionary strategy for their bioremediation examples. Willis showed DES also worked better on the chlorinated ethenes example than did the genetic algorithm. Yoon & Shoemaker (2001) showed that a real valued genetic algorithm does perform better than a binary valued genetic algorithm on a bioremediation problem with continuous variables.

**RISK ANALYSIS**

Because chlorinated ethenes are toxic chemicals, which are remediated at great expense, it is relevant to perform a risk analysis. Most risk analyses are done
deterministically. Benekos (2001) did a probabilistic risk assessment of the remediation of chlorinated ethenes using the CORDITE model. This study incorporates geological uncertainty, uncertainty in the spatial distribution of the microorganisms that influence the bioremediation process and individual human variability in health risks. The relative influence of the uncertainty in the spatial distribution of the microorganisms that affect the bioremediation process vs the influence of the uncertainty in the spatial distribution of the groundwater parameters (hydraulic conductivity), in the assessment of the risk estimates is also compared.

The risk analysis is performed for an example with a downstream drinking water well and a 100 year time horizon. The enhanced bioremediation only occurs for a few years at the beginning of the time horizon and brings the contaminant concentrations down to accepted maximum contaminant levels. The remaining years are necessary to assess the risk associated with the residual contaminant. The analysis computes upper bounds on risk for percentiles of both the aquifer uncertainty and population variability. This analysis is done for three population age categories: adult, adolescent, and child.

There have been prior studies coupling groundwater modelling to risk assessment (e.g. Pelmulder et al., 1996, and James & Oldenburg, 1997) A probabilistic risk assessment methodology is presented for incorporation of aquifer uncertainty and population variability into calculations of human health risk in the work of Maxwell et al. (1998, 1999); Maxwell & Kastenberg (1999). None of the prior studies considers bioremediation or the fact that the degradation product is also toxic. The earlier risk analysis studies model just one contaminant.

Our research differs from all prior research in that: (a) there are four contaminants rather than one; (b) enhanced bioremediation (including the effects of donor transport) is applied rather than pump and treat; (c) a stochastic sensitivity analysis is presented allowing the ranking of importance of the aquifer uncertain and population variable parameters; and (d) the impact of the contamination is studied and comparisons of the relative influence of aquifer uncertainty and population variability in the propagation of variability in the results are made for three population age categories: adults, adolescents and children.

SUMMARY AND CONCLUSIONS

Bioremediation of chlorinated ethenes is complicated by the number of toxic daughter products, the number of biological and chemical species involved in degradation, and the transport of all these species (which all have differing retardation coefficients). This overview describes the development of a numerically accurate 3-D transport model that incorporates the reactions between these species, sensitivity analysis and the application of the model to risk analysis. Such an analysis is very helpful in designing and understanding reductive dechlorination for in situ bioremediation of this complex problem.

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