

## MODELING NATURAL ATTENUATION AT THE PLATTSBURGH AIR FORCE BASE

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**Abstract:** A coupled biodegradation-redox transport model, BIOREDOX, was used to model the natural attenuation of BTEX and chlorinated ethenes at the Plattsburgh Air Force Base in New York. The model included representation of the redox-dependent biodegradation of TCE, DCE, and vinyl chloride, as well as the accumulation of chloride derived from these chlorinated ethene transformations. Redox-dependent biodegradation mechanisms represented in the model included oxidation, reductive dechlorination, and methanotrophic co-metabolism. Modeling of the redox zones downgradient from the LNAPL source was conducted by coupling BTEX oxidation with the reduction of inorganic electron acceptors (i.e. oxygen, nitrate, mineral-phase ferric hydroxides, sulfate, and carbon-dioxide). The production of dissolved ferrous iron and methane was also modeled. A unique visualization method for identifying redox-dependent transport mechanisms is presented. An innovative new approach for visually comparing field-measured concentrations to model predictions during the calibration process is also illustrated.

### INTRODUCTION

BIOREDOX (Carey et al., 1999a) is a public domain three-dimensional transport model, and is based on the MT3DMS model (Zheng, 1998). BIOREDOX is capable of representing coupled oxidation-reduction reactions between multiple electron donors and acceptors, and can simulate the influence of redox conditions, substrate concentrations, and inhibitor concentrations on the biotransformation rates and biodegradation pathways of organic pollutants. BIOREDOX can also represent straight-chain sequential transformations that occur during the anaerobic reductive dechlorination of chlorinated ethenes such as trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride. The governing equations and verification program for BIOREDOX are described by Carey et al. (1999a,b).

Full-scale field applications of coupled biodegradation-redox models have been limited in the past because suitable models were not readily available. This study presents a simple application of BIOREDOX to simulate the redox-dependent, natural attenuation of chlorinated ethenes at a full-scale field site. A former fire training area at the Plattsburgh Air Force Base was selected as the candidate site for this study because a general review of site conditions was available in the public domain (Wiedemeier et al., 1996). A detailed summary of the biodegradation reactions represented in this model are discussed, and two new

visualization methods for analyzing and presenting BIOREDOX model results are also demonstrated.

## **SITE SETTING**

Activities at the former fire training area (Site FT-002) at the Plattsburgh Air Force Base caused the development of a light nonaqueous-phase liquid (LNAPL) plume in the shallow sand aquifer below the site. Wiedemeier et al. (1996) present measured chemical concentrations for six monitoring well locations (referred to as stations A through F) situated on a transect along the primary flow path downgradient from the source area. Dissolved pollutants downgradient from the source area include benzene, toluene, ethylbenzene and xylene (BTEX), as well as TCE, DCE, and vinyl chloride.

Carey (1998) presents a SEQUENCE-BTEX/CAH radial diagram map for the site, which illustrates spatial trends in measured concentrations of total BTEX, TCE, DCE, vinyl chloride, and chloride downgradient from the source area, including relative changes between parent and daughter species. This radial diagram map shows that total BTEX and TCE concentrations decrease significantly downgradient from the source area. Carey (1998) also presents a SEQUENCE-Redox map, which indicates that conditions are strongly reducing downgradient from the source area, and become more oxidizing with increasing distance from the source.

## **NATURAL ATTENUATION MODELING**

The hydrogeochemical model for the site was developed based on data published by Wiedemeier et al. (1996). A simplified two-dimensional plan view model was used to represent groundwater flow and solute transport in the unconfined aquifer at the site. The objective of this application was to demonstrate the effects that redox-dependent biodegradation may have on simulated plume distributions. There was no attempt to calibrate the model biodegradation kinetics to match the simulated plumes to observed concentrations. Further refinement of the conceptual model, including consideration of vertical variations in solute concentrations and redox conditions, and calibration of the simulation model, is required before using this model for more detailed applications.

MODFLOW (McDonald and Harbaugh, 1988) was used to simulate the groundwater flow regime, and BIOREDOX was used to simulate the transport of organic and inorganic solutes in the aquifer. The model domain was oriented so that the principal directions of the coordinate axes were aligned with the principal direction of regional groundwater flow (i.e. northwest to southeast). The boundary conditions defined at the limits of the flow model domain were selected so that the model was capable of providing a general representation of horizontal groundwater flow in the aquifer. Descriptions of the model domain discretization, boundary conditions, and input properties are presented by Carey et al. (1999c).

Benzene, toluene, ethylbenzene, and xylene have widely varying biodegradabilities, sorption properties, and drinking water criteria. Although BIOREDOX is capable of representing the oxidation of multiple electron donors,

total BTEX was represented as one lumped solute for this study because there was not sufficient data available to model the individual BTEX constituents.

The transport simulation model represented the coupling between the oxidation of BTEX and the reduction of available electron acceptors, including oxygen, nitrate, mineral-phase ferric hydroxide coatings, and sulfate. It was assumed that carbon dioxide was non-limiting with respect to methanogenic activity. The model also simulated the production and transport of dissolved ferrous iron and methane. The coupling between ferrous iron oxidation (assumed to be an instantaneous reaction) and oxygen reduction was also represented because it may strongly influence the sequential anaerobic-aerobic treatment of chlorinated ethenes in groundwater (Carey et al., 1999c).

TCE was specified to undergo first-order sequential transformation to DCE in the iron-reducing, sulfate-reducing, and methanogenic zones. TCE degradation was assumed to be negligible in the aerobic and nitrate-reducing zones. DCE was assumed to undergo first-order sequential transformation to vinyl chloride only in the methanogenic zone. Vinyl chloride was assumed to undergo rapid first-order oxidation as a primary substrate in the aerobic and iron-reducing zones. Vinyl chloride was also assumed to undergo reductive dehalogenation as a secondary substrate in the methanogenic zone. The accumulation of chloride during the transformation of these chlorinated ethenes was also simulated.

Figure 1 illustrates the redox-dependent biodegradation mechanisms and reaction kinetics that were represented in the simulation model. Figure 2 shows the redox-dependent first-order reaction half-lives which were chosen for this demonstration study.

**Simulated BTEX Plume and Redox Zones.** BIODOX incorporates a unique visualization approach for identifying the simulated redox zones (Carey et al., 1999a). This form of redox mapping is important when evaluating simulations of the redox-dependent biodegradation of petroleum hydrocarbons and chlorinated solvents. Figure 3 presents the simulated redox zone distribution and BTEX concentration contours for the site, corresponding to the end of the 10 year simulation period. Figure 3 shows that BTEX is not present within the aerobic portion of the aquifer, which is consistent with the model input specification of aerobic BTEX oxidation as an instantaneous reaction (anaerobic BTEX oxidation was assumed to be a first-order reaction).

**Comparing Field-measured and Model Concentrations.** As part of any modeling exercise, it is necessary to compare model predictions to conditions observed in the field. For the Plattsburgh Air Force Base, one must compare the simulated concentrations for ten different solutes at six monitoring stations to the field-measured concentrations. It is also necessary to compare the simulated and observed trends between the parent species (TCE) and daughter products (DCE and vinyl chloride) at each monitoring station, to determine if the model is providing a reasonable representation of the natural bioattenuation mechanisms for TCE.

SEQUENCE radial diagrams may be used to provide an effective comparison between model predictions and field conditions. For demonstration purposes, Figures 4 and 5 show radial diagram maps that compare model and field-measured concentrations for the dissolved solutes at each monitoring station. An analysis of these two radial diagram maps may be conducted more readily than an analysis of the corresponding data table (which would consist of 120 data points).

## SUMMARY

This study shows how BIOREDOX may be used to evaluate the natural attenuation of petroleum hydrocarbons and chlorinated solvents at a full-scale field site. Innovative visualization methods for evaluating redox-dependent transport mechanisms, and for comparing model predictions to field-measured concentrations for a multispecies transport model, are demonstrated.

## REFERENCES

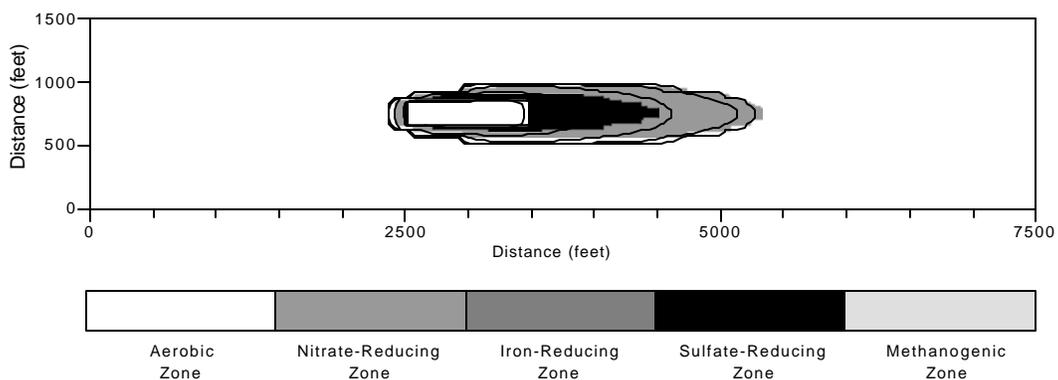
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	$CH_4$	$SO_4$	$Fe^{3+}$	$NO_3$	$O_2$		<i>Mechanism</i>	<i>Kinetics</i>
<i>BTEX</i>	■	■	■	■	■	■	Oxidation	Instantaneous
<i>TCE</i>	■	■	■	■	■	■	Oxidation	First-Order
<i>DCE</i>	■	■	■	■	■	■	$CH_4$ Co-metabolism	First-Order
<i>VC</i>	■	■	■	■	■	■	Dehalogenation	First-Order
$Fe^{2+}$	■	■	■	■	■	■	No Degradation	n/a
$CH_4$	■	■	■	■	■	■		

FIGURE 1. Redox-dependent biodegradation reaction mechanisms and kinetics that were simulated for the Plattsburgh Air Force Base model.

	$CH_4$	$SO_4$	$Fe^{3+}$	$NO_3$	$O_2$
<i>BTEX</i>	12	12	12	1	Inst.
<i>TCE</i>	6	6	6		2
<i>DCE</i>	6				2
<i>VC</i>	6		3		2   3
$Fe^{2+}$					Inst.
$CH_4$	24	24	24	24	2

FIGURE 2. Redox-dependent half-lives (in months) that were simulated for the first-order biodegradation reactions.



(Note - BTEX concentration contours of 0.001, 0.01, 0.1, 1, and 10 mg/L.)

FIGURE 3. Simulated BTEX plume and redox zones (t = 10 years).

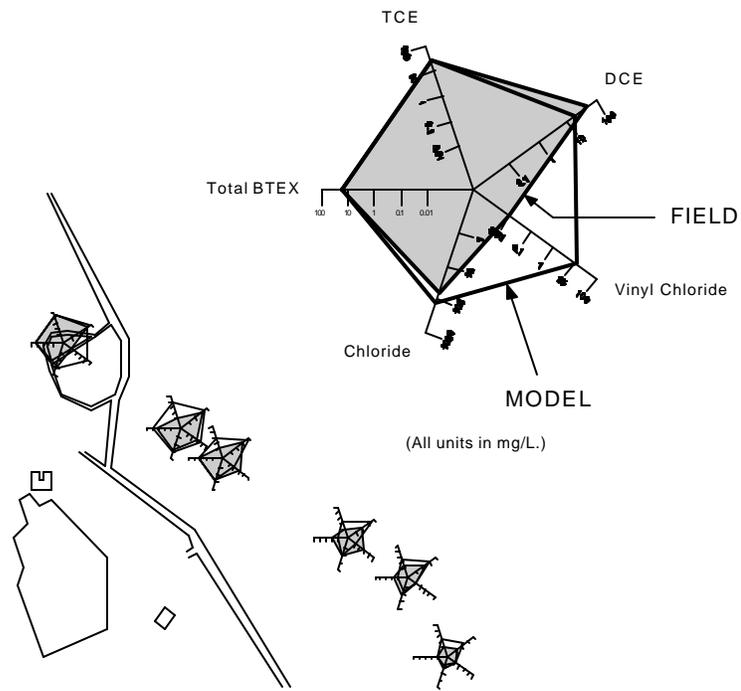


FIGURE 4. Comparison of field-measured and model predictions for BTEX, chlorinated ethene, and chloride concentrations.

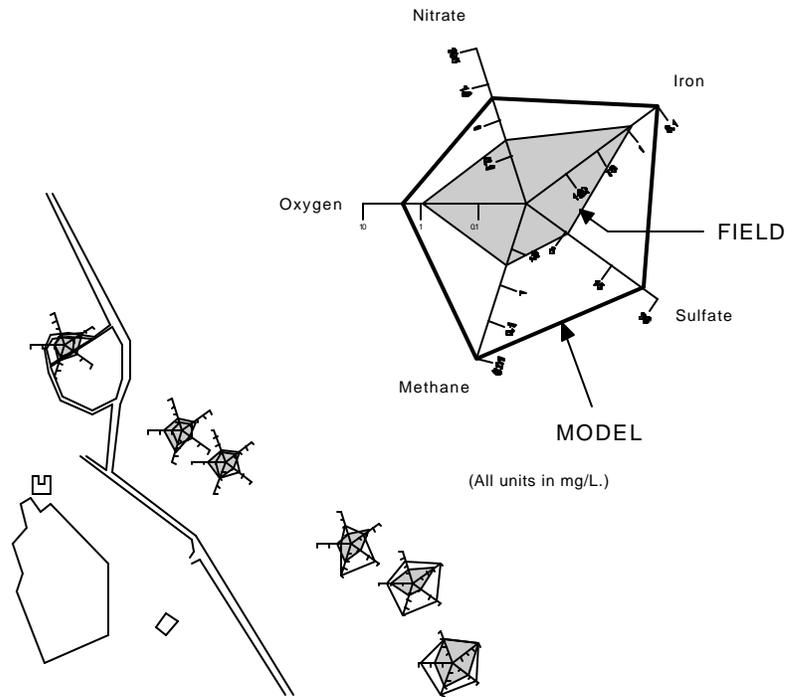


FIGURE 5. Comparison of field-measured and model predictions for redox indicator concentrations.