Coupled Biodegradation-Redox Modeling to Simulate Natural Attenuation Processes at the Plattsburgh Air Force Base (New York)

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ABSTRACT

A coupled biodegradation-redox transport model, BIOREDOX, is applied to evaluate the natural attenuation of BTEX and chlorinated ethenes at the former fire training area at the Plattsburgh Air Force Base in New York. BIOREDOX is used to simulate the development of redox zones downgradient from the source area by coupling BTEX oxidation with the reduction of inorganic electron acceptors. BIOREDOX is also used to simultaneously simulate the redox-dependent biodegradation of TCE, DCE, and vinyl chloride, as well as the accumulation of chloride derived from these chlorinated ethene transformations. The predicted outcomes for a two-dimensional integrated-depth model and a two-dimensional cross-section model were shown to be similar for the site-specific conditions assumed for this study.

INTRODUCTION

Model dimensionality is an important consideration when using coupled biodegradation-redox transport models to simulate the natural attenuation of petroleum hydrocarbons and chlorinated solvents. Representing these complex processes in three dimensions is ideal, but may also be prohibitively time-consuming and expensive, particularly for multicomponent simulations involving five to ten different solutes.

Using a two-dimensional simulation model to represent the natural attenuation of organic contaminants is a more economical approach, provided that the conceptual model is sufficiently representative of site conditions. Redox conditions may vary significantly with depth in an aquifer. Therefore, one must consider the differences between an integrated-depth single layer model (representing horizontal flow) and a cross-section model (representing horizontal and vertical flow) when selecting the model dimensionality for simulating redox-dependent processes.

This study presents an application of a coupled biodegradation-redox model, BIOREDOX (Carey et al., 1998a), for simulating the natural attenuation of petroleum hydrocarbons and chlorinated ethenes at a former fire training area at the Plattsburgh Air Force Base. Specifically, this study demonstrates the effects that redox-dependent biodegradation may have on simulated plume

distributions, and a comparison of the simulated plume distributions that were derived using a two-dimensional integrated-depth model and a two-dimensional cross-section model.

BACKGROUND

Intrinsic Biodegradation of BTEX. Petroleum hydrocarbons such as benzene, toluene, ethylbenzene, and xylene (BTEX) are generally utilized as primary substrates during the biodegradation process. The oxidation of a primary substrate results in an electron transfer from the substrate (also referred to as the electron donor) to available electron acceptors. This electron transfer results in the release of energy which is utilized for microbial metabolism. Typical electron acceptors available in groundwater, in the order of those that release the greatest energy to those that release the least energy, are as follows: dissolved oxygen, nitrate, manganese (IV) oxide and iron (III) hydroxide coatings on soil sediments, dissolved sulfate, and carbon dioxide. The long-term oxidation of BTEX depletes the supply of available electron acceptors in a step-wise, or sequential manner, so that the redox potential in groundwater becomes more reducing during the biodegradation process.

Intrinsic Biodegradation of Chlorinated Ethenes. The aerobic co-metabolism of chlorinated ethenes is generally of little significance unless a suitable electron donor (e.g. methane) is present (McCarty, 1997). However, it is possible for vinyl chloride to be oxidized under aerobic conditions, or under anaerobic conditions where iron (III) is the electron acceptor (Bradley and Chapelle, 1996). The principal mechanism involved in the anaerobic biodegradation of chlorinated ethenes is reductive dechlorination. The anaerobic reduction of PCE and TCE to ethene (through sequential intermediate products of DCE and vinyl chloride) has been observed at many sites. McCarty (1997) provides a general review of the redox-dependent biodegradability of chlorinated ethenes. In summary, the complete transformation from PCE and TCE to ethene will occur only under methanogenic conditions. Under less reducing conditions, PCE and TCE may be transformed to DCE, but will not be transformed further to vinyl chloride or ethene. Reductive dechlorination of these chlorinated ethenes will not occur in the nitrate-reducing zone.

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. (1997) provide a description of conditions observed at the site, which are summarized below.

The shallow aquifer consists of well-sorted, fine- to medium-grained sand with trace silt, and is underlain by relatively thick units of clay and glacial till. The aquifer has a saturated thickness of approximately 45 feet, an average horizontal hydraulic gradient of 0.01 foot per foot (ft/ft), an average hydraulic conductivity of 11.6 feet per day (ft/day), an effective porosity of 0.30, and an average groundwater velocity of approximately 140 feet per year. Groundwater flow below the

site is to the southeast. Because of low background concentrations of total organic carbon (TOC) in the aquifer, retardation is not considered to be an important transport process.

Figure 1 shows a site map which delineates the approximate extent of the LNAPL source area and the dissolved pollutant plume. The LNAPL source consists of jet fuel mixed predominantly with tetrachloroethene (PCE) and trichloroethene (TCE). Cis-1,2-dichloroethene (DCE) and vinyl chloride were not detected in the LNAPL. Dissolved pollutants downgradient from the source area include BTEX, TCE, DCE, vinyl chloride and ethene. Dissolved concentrations of BTEX and TCE in the source area were measured as high as 17 and 25 milligrams per liter (mg/L), respectively.

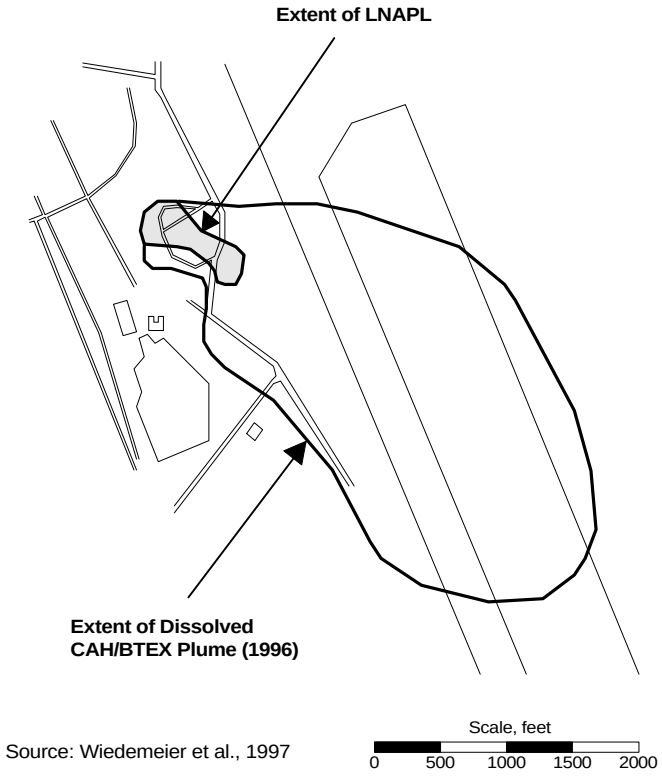

Figure 1 – Plattsburgh Air Force Base Site Map.

Upgradient from the site the aquifer is aerobic in nature, with background concentrations of oxygen, nitrate, and sulfate on the order of 10 mg/L, 10 mg/L, and 25 mg/L, respectively. Background concentrations of ferrous iron and methane (potential metabolic byproducts of microbially mediated oxidation-reduction reactions) are less than 0.05 mg/L and 0.001 mg/L, respectively. Measured concentrations of these electron acceptors and metabolic by-products indicate that conditions are strongly reducing within and downgradient from the source area.

NATURAL ATTENUATION MODELING

Two simulation models were developed to represent groundwater flow and solute transport in the unconfined aquifer at the site: a two-dimensional integrated-depth model and a two-dimensional cross-section model. The objectives of this application were to demonstrate the effects that redox-dependent biodegradation may have on simulated plume distributions, and to examine the effects of dimensionality on the simulation results. 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 measured solute concentrations and redox conditions, and calibration of the simulation models, is required before these models may be used for more detailed analyses.

MODFLOW (McDonald and Harbaugh, 1988) was used to simulate the groundwater flow regime. The model domains were 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 domains were selected so that the models provided a general representation of groundwater flow in the aquifer. Descriptions of the model domain discretization, boundary conditions, and input properties are presented by Carey et al. (1998b).

BIOREDOX was used to simulate the coupled oxidation-reduction reactions between organic electron donors and inorganic electron acceptors. BIOREDOX is a three-dimensional multicomponent transport program that is available in the public domain, and is based on the widely used MT3D model (Zheng, 1990). BIOREDOX was designed with the necessary flexibility so that it may be applied to model the influence of redox conditions, substrate concentrations, and/or inhibitor concentrations on the biotransformation rates and pathways of petroleum hydrocarbons and chlorinated solvents. 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 BIOREDOX governing equations and verification program are described by Carey et al. (1998a,c).

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 models 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 using solubility limits that were determined based on maximum measured concentrations of these metabolic byproducts. 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., 1998b).

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, but due to simplifications in the model this oxidation reaction was not coupled to the reduction of the respective electron acceptors. Vinyl chloride was also assumed to undergo reductive dehalogenation as a secondary substrate in the methanogenic zone. TCE, DCE, and vinyl chloride were assumed to undergo rapid methanotrophic co-metabolism in the aerobic zone if methane was present at concentrations greater than 0.001 mg/L. The accumulation of chloride during the transformation of these chlorinated ethenes was also simulated.

Simulated BTEX Plume and Redox Zones. BIOREDOX incorporates a unique visualization approach for identifying the simulated redox zones (Carey et al., 1998b). This form of redox mapping is important when evaluating simulations of the redox-dependent biodegradation of petroleum hydrocarbons and chlorinated solvents. Figure 2 presents the simulated redox zone distribution and BTEX concentration contours for the integrated-depth and cross-section models, corresponding to the end of the 10 year simulation period. Figure 2 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).

A comparison of the simulated lengths of the BTEX plumes and individual redox zones along the primary flow path downgradient from the source area, as shown in Figure 2, indicates that the integrated-depth and cross-section models predict a similar outcome for the natural attenuation of BTEX. This similarity is based on the site-specific conditions that were assumed for this model scenario. This finding does not imply that these two different model representations will result in similar predictions for other sites.

Simulated TCE Plume and Redox Zones. Figure 3 illustrates the simulated distributions for TCE for the integrated-depth and cross-section models. The simulated redox zones are included in each of these figures to allow for an interpretation of the effects of redox-dependent biodegradation mechanisms on the shapes of the individual solvent plumes. For example, the 0.1 mg/L TCE concentration contours shown in Figure 3 illustrates that a concentration gradient exists between the more reducing portion of the aquifer where TCE biodegradation is occurring, and the aerobic and nitrate-reducing portions of the aquifer, where TCE degradation was assumed to be negligible. These figures also indicate that the different simulation models predict a similar outcome for the natural attenuation of TCE. Comparison of the simulated distributions of DCE and vinyl chloride (not shown here) confirm that the two simulations models also provide similar results for these daughter products.

Simulated Electron Acceptor and Metabolic By-Product Plumes. Figure 4 shows the oxygen, nitrate, dissolved ferrous iron, and methane plumes that were simulated using the cross-section model. The results of these simulations are consistent with the simulated redox zone distributions and the redox-dependent biodegradation processes that influence the simulated BTEX and TCE plumes shown in Figures 2 and 3. These results are also similar to the distributions that were predicted by the integrated-depth model (not shown here).

SUMMARY

This study shows an application of a coupled biodegradation-redox model for simulating the natural attenuation of petroleum hydrocarbons and chlorinated solvents at the Plattsburgh Air Force Base. The influence of coupled oxidation-reduction reactions and redox-dependent biodegradation mechanisms on simulated plume behavior is shown, and the outcomes predicted by a two-dimensional integrated-depth model and a two-dimensional cross-section model were shown to be similar for the site-specific conditions assumed for this scenario.

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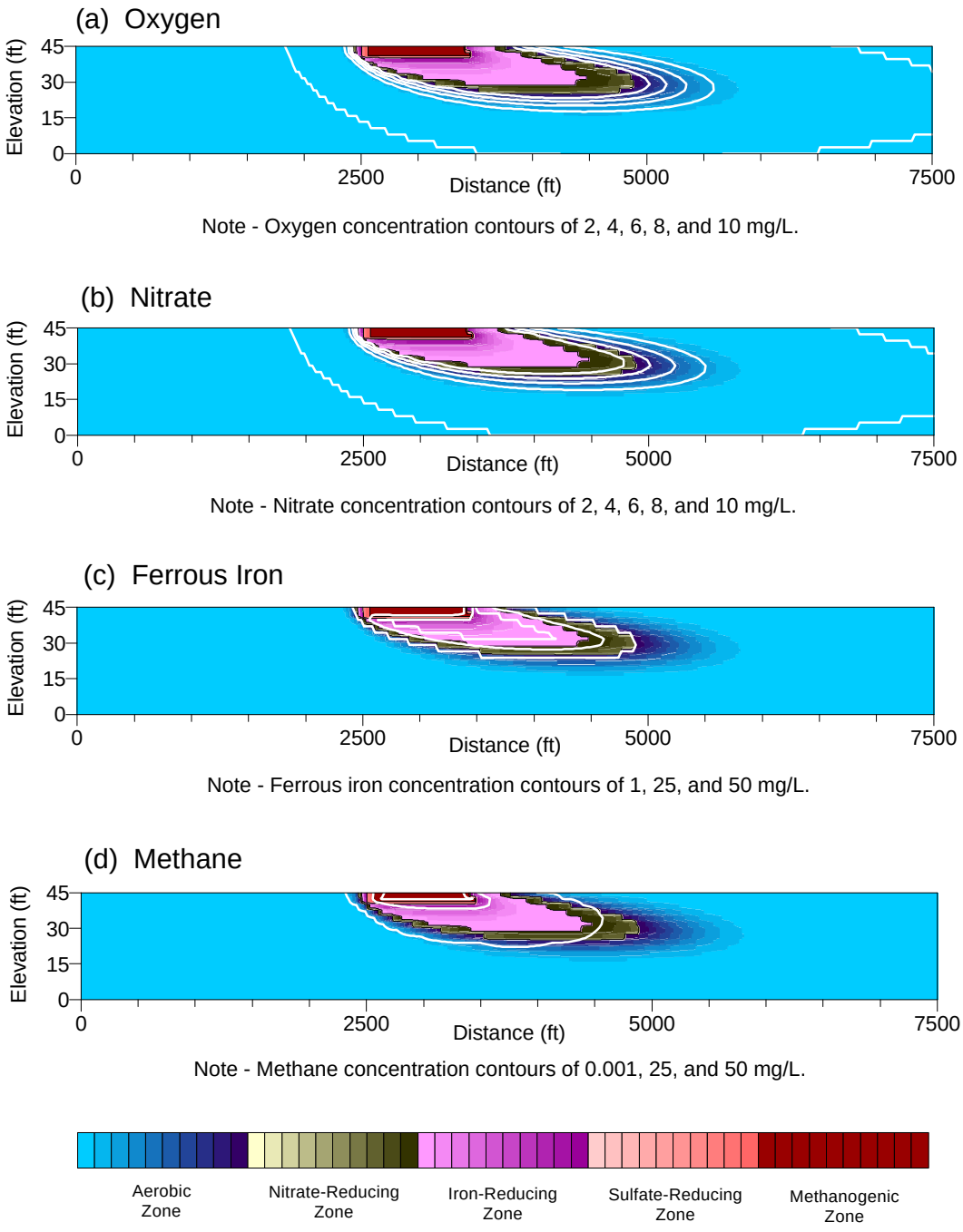

FIGURE 4. Simulated Electron Acceptor, Metabolic By-Product and Redox Zone Plumes.

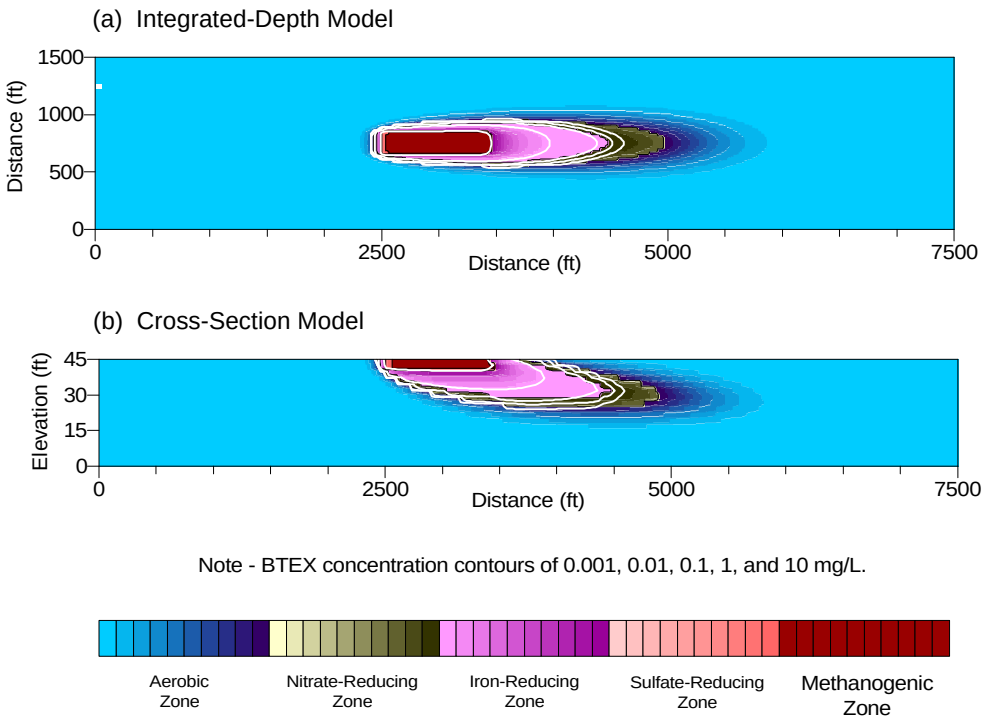

FIGURE 2. Simulated BTEX and Redox Zone Plumes.

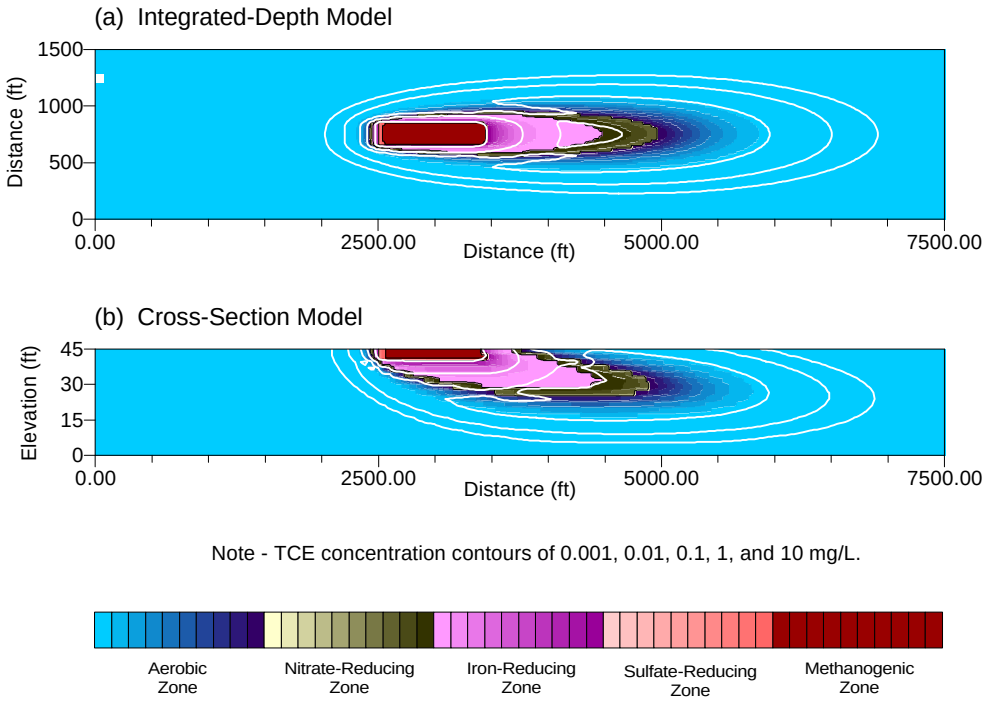

FIGURE 3. Simulated TCE and Redox Zone Plumes.