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Natural attenuation of fuel hydrocarbon contaminants: Correlation of biodegradation with hydraulic conductivity in a field case study

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ABSTRACT

Two biodegradation models are developed to represent natural attenuation of fuel-hydrocarbon contaminants as observed in a comprehensive natural-gradient tracer test in a heterogeneous aquifer on the Columbus Air Force Base in Mississippi, USA. The first, a first-order mass loss model, describes the irreversible losses of BTEX and its individual components, i.e., benzene (B), toluene (T), ethyl benzene (E), and xylene (X). The second, a reactive pathway model, describes sequential degradation pathways for BTEX utilizing multiple electron acceptors, including oxygen, nitrate, iron and sulfate, and via methanogenesis. The heterogeneous aquifer is represented by multiple hydraulic conductivity (K) zones delineated on the basis of numerous flowmeter K measurements. A direct propagation artificial neural network (DPN) is used as an inverse modeling tool to estimate the biodegradation rate constants associated with each of the K zones. In both the mass loss model and the reactive pathway model, the biodegradation rate constants show an increasing trend with the hydraulic conductivity. The finding of correlation between biodegradation kinetics and hydraulic conductivity distributions is of general interest and relevance to characterization and modeling of natural attenuation of hydrocarbons in other petroleum-product contaminated sites.

INTRODUCTION

In providing proof of natural attenuation of contaminants in the subsurface, field data combined with models are needed to link decreases in contaminant concentrations to the underlying mass loss mechanisms (National Research Council, 2000). Numerical models usually simulate sequential

aerobic/anaerobic biodegradation at petroleum hydrocarbon sites where the flow field is two- or three-dimensional, with the degradation rate coefficient assumed uniform.

In contrast to the uniform rate approach, biodegradation rates in the field are usually spatially and/or temporally variable because of chemical and physical variations in the aquifer environment. Factors that contribute to the non-uniform degradation include: (1) availability of electron acceptors and nutrients (Allen-King et al., 1994), (2) the presence of toxic compound, and (3) aquifer redox (Lyngkilde and Christensen, 1992; Cozzarelli et al., 1999) or pH environments. These factors are in turn affected by the aquifer physical heterogeneity. A few field and laboratory studies have provided evidence for permeability heterogeneity affecting biodegradation rates (Scholl, 2000). Biodegradation rates were observed to vary spatially over the length of a BTEX plume, with the presence of clay lenses in the sandy aquifer thought to be one contributing factor (Hunt et al., 1998). In a detailed large-scale laboratory experiment (Murphy et al., 1997), enhanced microbial growth was observed contributing to prolonged

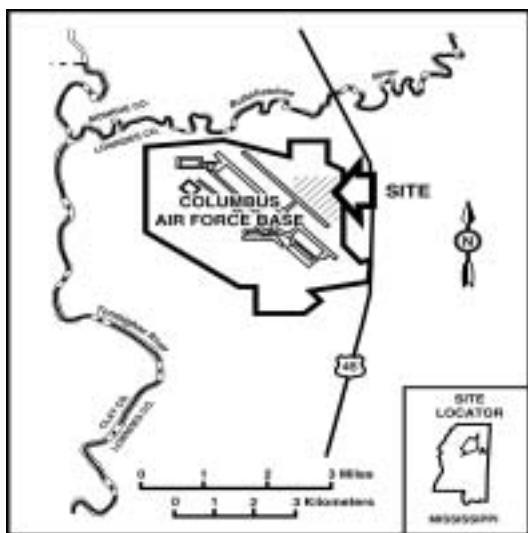


Figure 1. Location map of the natural attenuation study (NATS) site at the Columbus Air Force Base, Mississippi. (After Boggs, et al., 1990).

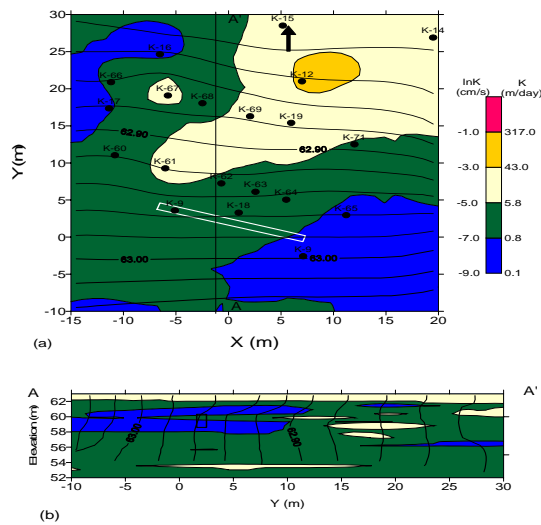


Figure 2. The hydraulic conductivity (m/day) and head (m) distributions: (a) at the elevation of 59.75 m, and (b) cross section A-A' (modified from Julian et al., 2001). The rectangle indicates the source location.

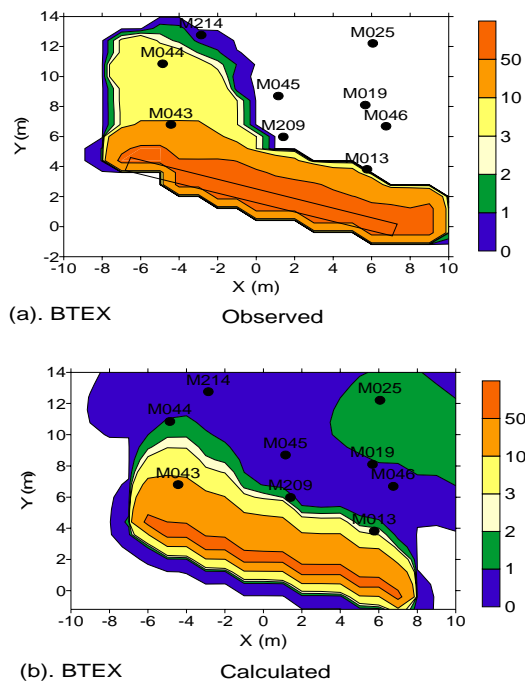


Figure 3. Observed and calculated BTEX plumes (concentration in mg/L) at 100 days after the release (Dec 7-8, 1995): (a) Observed; and (b) Calculated.

availability of substrate and oxygen for degradation downgradient of low permeability inclusions. Lower microbial activity was found in low-permeability aquifer sediments as opposed to higher permeability sediments (Aelion, 1996).

For a heterogeneous aquifer, biodegradation would have been better characterized with an approach of varied degradation rates. However, estimation of spatial and/or temporal variations in attenuation processes is computationally demanding. First, the kinetic rate coefficients may need to be optimized for multiple components. Second, the model domain needs to be discretized into different parameter zones, leading to increased computational burdens. The effort of quantifying spatial and/or temporal variations of degradation is essentially equivalent to solving a complex parameter estimation problem.

The NATS site at the Columbus Air Force Base in Mississippi, USA (Figure 1) is the former Macrodispersion Experiment (MADE) site known for its heterogeneous aquifer system (Boggs et al., 1990; Julian et al., 2001). It represents one of the most comprehensive and complex field experiment sites to date on natural attenuation of fuel-hydrocarbon contaminants (Stauffer et al., 1997). In this study, the model domain was divided into multiple parameter zones based on field observation data, to better simulate the contaminant degradation. In estimation of kinetic rate coefficients, this study uses a novel neural optimization algorithm called Direct Propagation Network (DPN). The DPN was interfaced with MT3D (Zheng, 1990) for mass loss modeling and with RT3D (Clement, 1998) for reactive pathway modeling. DPN treats the parameters to be estimated as input and the difference between calculated values and observation data as output. The coupling of DPN with the mass loss model and with the pathway model for parameter estimation was stopped when the parameters obtained from the DPN model resulted in the closest match between the calculated and observed concentrations.

BIOGEOCHEMICAL MODELS

The NATS site is characterized by a high degree of heterogeneity in the underlying alluvial aquifer (Figure 2). This study involves two types of natural attenuation modeling: the BTEX mass loss model and BTEX reactive pathway model. The BTEX mass loss model is a simple degradation model using the concentration changes of electron donors

BTEX, B, T, E and X to quantify the degradation rates. The BTEX reactive pathway model describes the biodegradation processes at the NATS site as microbially-mediated BTEX degradation utilizing oxygen, nitrate, ferric iron, sulfate, and via methanogenesis. The observed biodegradation processes at the NATS site are microbially-mediated BTEX degradation utilizing oxygen, nitrate, ferric iron, sulfate, and methanogenesis. Detailed discussions about the sequential model of BTEX degradation is found in Clement (1998), Lu et al. (1999), Zheng and Bennett (2002), and Lu and Zheng (2004).

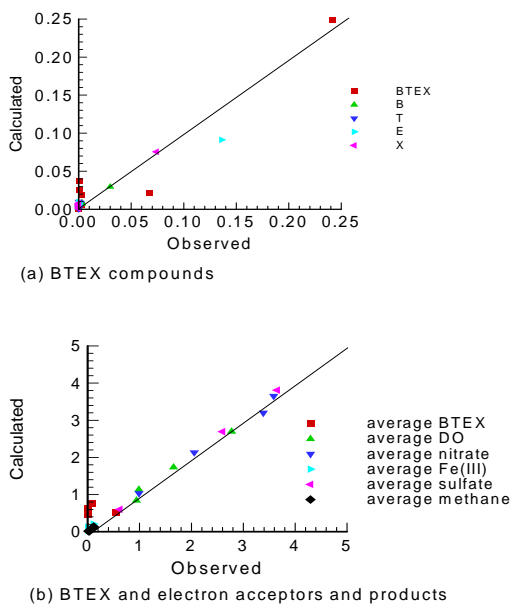


Figure 4. Observed and calculated concentrations (mg/L) at 100 days after the source release: (a) BTEX compound degradation; and (b) BTEX degradation via electron accepting processes.

In the BTEX reactive pathway model, the total amount of the B, T, E, and X is summed up and simulated as a lump term BTEX. This is based on the similar properties among these benzene series products. The similar stoichiometry for the degradation of all these components yields very small differences in the mass balance calculation. For example, the relative difference of using benzene to approximate xylene degradation via sulfate reduction is about 1.9%.

BTEX compounds comprise the majority of the dissolved organic mass in equilibrium with water in fuel hydrocarbon field sites. Studies of the BTEX solubility show that BTEX dominated the aqueous phase of the total dissolved mass from the JP-4 fuel, although it represents only a small fraction of the light non-aqueous phase liquid (LNAPL) mass (Wiedemeier et al., 1999). For the NATS site, the components of the LNAPL source are listed in Table 1. The BTEX compounds consist as high as 96.7% of the total dissolved mass in the JP-4 fuel at the NATS site.

Table 1. Composition and Chemical Properties of the LNAPL Source for the NATS Experiment[†]

LNAPL Component	Pure phase Solubility (mg/L)	Molecular Weight (g/mol)	Percent of NAPL (by weight)	Mole fraction	Effective solubility (mg/L) ^{†‡}
Benzene	1790	78.1	0.05	0.0008	1.494
Toluene	500	92.1	6.6	0.0935	46.727
Ethylbenzene	165	106.7	7.1	0.0868	14.318
p-xylene	185	106.7	6.9	0.0843	15.602
Naphthalene	34	128.3	7.8	0.0793	2.698
Decane (Inert)	0.009	142.3	71.5	0.6553	0.006
Total			99.95	1	80.845

Note: [†]Data source: Boggs et al., 1995. [‡]Total BTEX effective solubility = 78.141 mg/L, equivalent to 96.7% of the total effective solubility.

The BTEX can be lost through the volatilization of BTEX from groundwater into soil gas. The loss of BTEX through volatilization is assumed to be negligible in the model. Volatilization of BTEX compounds from groundwater is a relatively slow process because of the small surface area of the groundwater flow system exposed to soil gas. Chiang et al. (1989) demonstrated that less than 5% of the mass of dissolved BTEX is lost to volatilization in the saturated ground water environment. For plumes located more than

one meter below the water table, very little mass will be lost due to volatilization (Rivett, 1995). The factors that hinder the volatilization includes the downward groundwater gradient in the vicinity of the water table (Rivett, 1995) and slow process of vapor transport across the capillary fringe (McCarthy and Johnson, 1992). Because of this, the impact of volatilization on dissolved contaminant reduction can generally be assumed to be negligible (Wiedemeier et al., 1999).

It is noted that the bioavailable Fe^{3+} concentration is consumed in biodegradation (Wiedemeier et al., 1999). The bioavailable Fe^{3+} is related to the solid Fe(III). Specifically, the best forms of Fe(III) for microbiological reduction are poorly crystalline Fe(III) oxyhydroxides, Fe(III) hydroxides, and Fe(III) oxides (Lovley, 1991). Total Fe(III) concentrations as determined through common laboratory techniques do not have much relevance, because without knowing the degree of crystallinity of the iron it is not possible to determine how much of the iron is available to microorganisms (Wiedemeier et al., 1999). Since the concentration of Fe^{3+} cannot be measured under normal field conditions (Wiedemeier et al., 1995), in the model Fe^{3+} was replaced with Fe^{2+} "assimilative capacity terms" for iron reduction. Similarly, CO_2 is also quantified through CH_4 capacity term. More detailed discussion is provided in Lu et al. (1999).

NUMERICAL SIMULATIONS

The modeling of the fate and transport of BTEX at the NATS site was initialized with the data collected on December 7, 1995 (Snapshot 0), when JP-4 jet fuel was released. A complete set of field observation data (100 days after the release of contaminants), referred to as Snapshot 2, was used for model calibration. The flow model of the aquifer, assumed to be at steady state, was taken as a submodel from a larger scale model for the entire MADE site (Julian et al., 2001). Sorption processes were ignored because background total organic carbon contents for 50 samples of alluvium ranged from 0.02 to 0.06% by weight, resulting in very low retardation estimates within the range of uncertainty.

Figure 2 shows the model domain and the location of the source trench. A three-dimensional finite-difference grid of 50 rows, 35 columns, and 22 layers was used for spatial discretization, with each model cell 0.8 m long by 1.0 m wide by 0.5 m high. The transport boundary conditions are: no mass flux at the bottom, eastern, and western boundaries, specified concentration at the southern boundary, and specified mass flux at the top and northern boundaries. The concentrations of BTEX, oxygen, nitrate, ferrous iron, sulfate, and methane were set at the southern (upstream) boundary equal to the concentrations interpolated from the measured background concentrations. At the northern (downstream) boundaries, the solutes were allowed to move freely out of the flow domain. The model domain was divided into different parameter zones, each of which was associated with a uniform degradation rate constant and hydraulic conductivity. Parameter zones were delineated on the basis of the flowmeter borehole locations and multi-level sampler locations.

RESULTS AND DISCUSSIONS

The reactive transport simulations used Snapshot 0 as the initial conditions. The concentration of BTEX

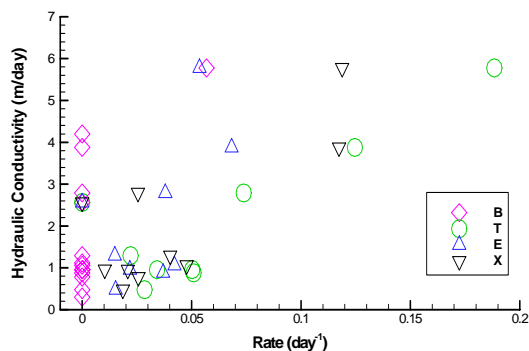


Figure 5. The hydraulic conductivity and the calculated BTEX degradation rates at 35 days after the source release.

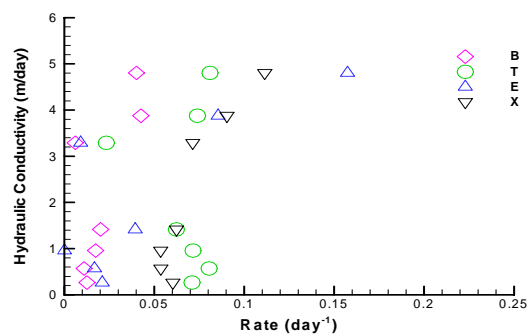


Figure 6. The hydraulic conductivity and the calculated BTEX degradation rates at 100 days after the source release.

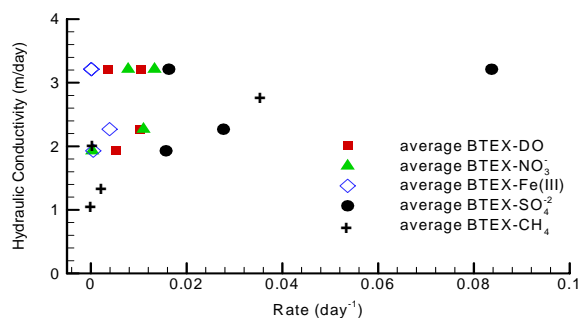


Figure 7. Hydraulic conductivity and the calculated rate constants of BTEX degradation via electron accepting processes at 100 days after the source release.

with 0.075, 0.020, 0.062, 0.039, and 0.062 day⁻¹ for BTEX, B, T, E, and X, respectively. They decrease in the order of BTEX, X, T, E and B. These results are consistent with the values from the literature (Wiedemeier et al., 1996).

The dependency of degradation rate constants on the hydraulic conductivity is confirmed with a stronger trend in the second model (reactive pathway model) (Figure 7), in which BTEX degradation with electron acceptors dissolved oxygen (DO), nitrate, ferric iron, sulfate, and degradation product methane was simulated. The match between the simulated concentrations and observed data is shown in Figure 4b. The first-order rate constants for electron accepting degradation are averaged as 0.0074, 0.0081, 0.0012, 0.0359, and 0.0097 day⁻¹ for aerobic, nitrate reduction, iron (III) reduction, sulfate reduction and methanogenesis. Sulfate reduction is the dominant process, followed by methanogenesis, nitrate reduction, and aerobic reduction. Iron reduction is ranked the lowest.

CONCLUSIONS

In a natural attenuation modeling study, usually there are multiple rate coefficient parameters to be estimated through model calibration. In addition, the model domain may need to be divided into different zones to characterize the heterogeneous nature of the aquifer. Thus modeling of natural attenuation processes becomes a complex parameter estimation problem. In this study, a novel optimization algorithm derived from artificial neural networks, called Direct Propagation Network (DPN), is used for parameter estimation.

Comparison of the calibrated model results with the observed field data shows that the natural attenuation models developed in this work reproduce the field data reasonably well (Figures 3 and 4), in terms of both overall plume patterns and the front positions of the plumes. The degradation rate coefficients of BTEX, benzene, toluene, ethyl benzene, and xylene vary from 0.00 to 0.157 day⁻¹. The calculated reaction rate coefficients (as determined from model calibration) are 0.075, 0.020, 0.062, 0.039, and 0.062 day⁻¹ for the degradation of BTEX, benzene, toluene, ethyl benzene, and xylene. The averaged values of the first-order rate constants for electron accepting degradation are 0.0074, 0.0081, 0.0012, 0.0359, and 0.0097 day⁻¹ for aerobic, nitrate reduction, iron (III) reduction, sulfate reduction and methanogenesis. The mass loss rates for BTEX and compounds show an increasing trend with the hydraulic conductivity (Figures 5 and 6). A similar trend for BTEX degradation via electron accepting processes is also found (Figure 7). The finding represents one of the first of its kind in characterizing natural attenuation of hydrocarbons in a heterogeneous aquifer. The results and insights obtained from this study as well as the parameter estimation procedure are of general interest and relevance, since the NATS site is representative of many petroleum-product contaminated sites with highly heterogeneous aquifers.

prior to Snapshot 0 was not detected in the source trench area. Elevated BTEX concentrations were observed away from the source on the downstream side. Figure 3 shows the simulation result at the time of Snapshot 2 for the first model (BTEX mass loss model) assuming first-order degradation of BTEX compounds, in comparison with the observed data. The match between the calculated and observed BTEX and components is also plotted in Figure 4a. The degradation-rate constants show an approximately linear trend with hydraulic conductivity for BTEX, B, T, E, and X, respectively (Figures 5, 6). The degradation-rate constants are generally higher in aquifer zones where the hydraulic conductivities are higher. This may suggest the conditions under which microbes have adapted to the environment. The degradation-rate constants vary from 0.00 to 0.157 day⁻¹. Their means are in the range of 0.020 to 0.064 day⁻¹,

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