

**Competition Between Chemical
and Physical Processes in
Bioremediation**

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Competition Between Chemical and Physical Processes in Bioremediation

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ABSTRACT

The performance of an in-situ groundwater remediation project is a complicated function of many factors, including subsurface flow rates and patterns, diffusion/dispersion, rate of contamination from the source, retardation and rate of degradation of the contaminant(s), availability of co-reactants for degradation, etc. The complexity of the interactions between these phenomena makes it difficult to interpret macroscopic behavior, e.g. variation in levels of contamination in an extraction well, or to predict field-scale performance from small-scale data.

This work illustrates the use of ParSSim, a parallel simulator of subsurface flow, transport and reaction, to elucidate the mechanisms that control performance of a intrinsic bioremediation project. The coupling of the chemical and physical processes leads to rich and sometimes counterintuitive behavior. For example, an increased dispersivity can lead to higher contaminant concentrations. Different chemical/physical factors may have the same qualitative effects on the concentration of contaminant reaching an observation well, and we illustrate how simulation can be used to discriminate between these factors. Finally we illustrate the use of the simulator to quantify biogeochemical "domains of influence", the regions of parameter space in which a particular reaction or mechanism dominates the process. Such knowledge is valuable in evaluating alternative remediation strategies.

INTRODUCTION

Spills or leaks of organic chemicals to the environment frequently result in the contamination of subsurface soils and groundwater. Many of these pollutants are only slightly soluble in water and thus may exist as non-aqueous phase liquid (NAPL). Because of its low solubility in the water, the presence of NAPL in the subsurface represents a potential long-term contaminant source (Pinder, 1982; Baehr, 1987). Documentation of the existence of NAPL in aquifer systems is growing (Atwater, 1984; Cohen et. al., 1987; Feenstra and Coburn, 1986), and methods for efficiently remediating these sites have been investigated intensively in the past few years.

In the unsaturated zone, entrapped organic chemicals can volatilize and be transported by diffusion or convection in the vapor phase or they can dissolve into infiltrating surface precipitation (Hinchee and Reisinger, 1987). The focus of this work is upon NAPL trapped in the saturated zone, which can partition directly into the aqueous phase (Mackay et. al., 1985). This partitioning reaction is a cause of groundwater contamination as well as the basis for the commonly applied pump-and-treat remediation process.

Several models have been developed to describe multiphase flow of organic contaminants in the subsurface with the exchange of organic mass between fluid phases (Abriola and Pinder, 1985a, b; Corapcioglu and Baehr, 1987; Sleep and Sykes, 1989; Baehr, 1987; Silka, 1986; Falta et. al., 1989; Dorgarten and Tsang, 1990). Most of these utilize the assumption of local equilibrium to describe the extent of partitioning between NAPL and the aqueous phase. The local equilibrium assumption implies that the concentrations of contaminant in each phase at a given spatial location can be described by thermodynamic partitioning relationships, and that the concentration in one phase determines the concentration in other phases.

A non-equilibrium description may be required for characterization of fluid-fluid mass transfer for some hydrodynamic regimes. In a laboratory study, Geller and Hunt (1989) found that concentrations of benzene and NAPL downstream of a large NAPL blob were significantly below thermodynamic equilibrium levels. Many investigators have reported that local equilibrium conditions were not obtained for sorption in column and field tests (Miller and Weber, 1986; Valocchi, 1988, Goltz and Roberts, 1988).

A growing body of field data indicates that concentration of NAPL in groundwater at contamination sites containing residual levels of NAPL is lower than their equilibrium values (Mackay et. al., 1985; Schwillie, 1975; Feenstra and Coburn, 1986).

Powers et al. (1991) presented a theoretical study of the significance of non-equilibrium dissolution of NAPL in subsurface systems. A one-dimensional convection-dispersion mass balance equation incorporating a first-order inter-phase mass transfer rate relationship and temporal changes in blob configuration was used to model this system. Analytical and numerical methods were employed to examine the steady state and transient behavior of the system under a variety of hypothetical aquifer conditions and remediation schemes. Sensitivity of the model to several parameters including mass transfer coefficient, blobs size and shape, and Darcy velocity was explored. Results of the theoretical assessment indicated that non-equilibrium effects could play a significant role in some contamination scenarios, primarily for large blob size and relatively high velocities.

In light of these findings a kinetic NAPL dissolution model has been used in this simulation study of the pump-and-treat remediation process. In addition to applying an accurate mathematical model for the mass transfer rate between NAPL and aqueous phase, Pope (1997) noted the importance of a large number of operational parameters. These include the number and location of injection, extraction, and monitoring wells and hydraulic control wells; pump rates for injection and extraction wells; screened interval in each well; concentrations of all chemical or biological species injected in each well as a function of time; and location and frequency of sampling points in the monitoring wells and/or multi-level samplers. Aquifer characterization leads to a second major category of modeling parameters which include permeability and porosity distribution of the aquifer formation; initial 3D distribution of the water, air, and NAPL saturations; geochemical properties of the water and soil (cation exchange); physical soil properties (e.g., capillary pressure, relative permeability); biological properties of the water and soil; and natural hydraulic gradient in the aquifer.

In the remainder of this section we present the equations describing the physical and chemical phenomena of interest, our strategy for solving these equations, and the structure of our parameter investigation.

Governing equations

The mathematical description of the NAPL contamination and remediation process studied here consists of flow, transport and reaction kinetics equations. These are:

$$\text{Single-phase incompressible flow:} \quad \nabla \bullet \mathbf{u} = q \quad \dots\dots\dots (1)$$

$$\text{Mass conservation of chemical species } i: \quad \phi \frac{\partial C_i}{\partial t} + \nabla \bullet (\mathbf{u} C_i - \mathbf{D} \nabla C_i) = \phi R_i + q_i \quad \dots\dots\dots (2)$$

$$\text{Darcy's Law:} \quad \mathbf{u} = -\frac{k}{\mu} \nabla \Psi \quad \dots\dots\dots (3)$$

$$\text{diffusion/dispersion tensor:} \quad \mathbf{D}(\mathbf{u}) = \phi D_{mol} \mathbf{I} + |\mathbf{u}| (D_{long} \mathbf{E}(\mathbf{u}) + D_{trans} (\mathbf{I} - \mathbf{E}(\mathbf{u}))) \dots (4)$$

$$\text{NAPL dissolution rate:} \quad R_{diss} = k_{diss} C_{imm} (K - C_{NAPL}) \quad \dots\dots\dots (5)$$

$$\text{NAPL biodegradation rate:} \quad R_{deg} = k_{EA} C_{mic} \frac{C_{NAPL}}{H_{NAPL} + C_{NAPL}} \frac{C_{EA}}{H_{EA} + C_{EA}} \quad \dots\dots\dots (6)$$

In these equations, \mathbf{u} is the fluid velocity, q incorporates well injection and extraction rates, μ is the fluid viscosity, k and ϕ are the permeability and porosity of the aquifer, and $\nabla \Psi$ is the potential gradient. The concentration of specie i is C_i , and R_i represents the rate of creation/removal of species i due to chemical reactions and interphase mass transfer. \mathbf{D} is diffusion/dispersion tensor, defined in terms of the molecular diffusion coefficient D_{mol} , the longitudinal dispersion coefficient D_{long} , the transverse dispersion coefficient D_{trans} and the identity tensor \mathbf{I} . $\mathbf{E}(\mathbf{u})$ is the tensor that projects onto the \mathbf{u} direction and whose (i,j) component is $\mathbf{E}_{ij} = u_i u_j / |\mathbf{u}|^2$. The concentration of the immobile NAPL phase is C_{imm} , measured on a unit pore volume basis. The rate constant for dissolution is k_{diss} , and the equilibrium concentration of NAPL in the aqueous phase is K . The rate constant for biodegradation of dissolved NAPL by means of electron acceptor EA is k_{EA} , and the half-saturation constant for species i in the Monod kinetics expression is H_i . For immobile components, the flux terms in the mass balance equation vanish.

Numerical Solution

Numerical solutions to these equations were obtained with ParSSim, a simulator for the incompressible, single-phase flow and reactive transport of subsurface fluids through a heterogeneous porous medium of somewhat irregular geometry. ParSSim is also capable of simulating the decay of radioactive tracers or contaminants in the subsurface, linear adsorption, wells and bio-remediation, as well

as arbitrary number of biogeochemical reactions between species in an arbitrary number of mineral and fluid phases (Saaf et al, 1996; Wheeler et al, 1996).

The simulator runs on single processors as well as on massively parallel, distributed memory computers and PC clusters. Results presented here were obtained on eight nodes of an IBM SP2 at the Texas Institute for Computational and Applied Mathematics. The message-passing interface (MPI) is used for communications between processors. The domain decomposition method is used to compute in parallel: the grid is divided into sub-domains, one for each parallel processor. Each sub-domain is given roughly the same number of gridblocks. Each processor is responsible for the simulation for the gridblocks owned by this processor or sub-domain. The individual processors send information to each other during the computation for the solution of the coupled underlying linear equations. ParSSim employs a locally conservative, mixed finite element method to discretize the flow equation. The Characteristics-Mixed Finite Element Method (CMM) and Godunov Mixed Method are used to compute the mass transport (Arbogast et al., 1992; Arbogast and Wheeler, 1995, Dawson, 1991).

The coupled flow and transport equations are solved using operator splitting. First, the mass conservation mixed finite element approximation for flow is solved implicitly for velocity using the Glowinski-Wheeler domain decomposition method (Glowinski and Wheeler, 1988) in parallel. This step is independent of the transport calculation and may have an independent time step size. The computed velocity field is passed to the transport calculation, which solves for concentrations of mobile and immobile species. This step is done independently using a time-splitting technique, that is, the advection and chemical reactions are solved explicitly first, and diffusion/dispersion is solved implicitly thereafter (Arbogast and Wheeler, 1993; Dawson and Wheeler, 1988; Dawson and Wheeler, 1992).

Problem Definition

Many of the simulation studies for remediation processes to date have been done in two dimensions and assumed homogeneity. The latter are not realistic for full-scale remediation projects. In this work, we focus on three dimensions and a heterogeneous aquifer. The NAPL is dispersed in the saturated zone as small immovable blobs. We examine the effects of dispersion, well injection rate,

heterogeneity of the field, and the rates of dissolution and biodegradation. The coupling between these parameters is of particular interest, motivated by the following inverse problem. Suppose that a remediation process has been designed and implemented, and that the data collected to date from a monitoring well differ from expected values. Given that the expectations are based on uncertain input (aquifer characterization, location and concentration of NAPL phase, chemical rate constants, etc.), what can be inferred about the performance of the process? How effective will it be in future? How efficient? What operating parameters, if any, should be changed to improve it? Obtaining a good engineering understanding of such a process requires not only a sound mathematical model, but also some insight into the couplings underlying the field observations. Providing this insight is one objective of this work.

The simulations reported herein are for a conceptual, representative aquifer, not a specific remediation site. We define a base case from which the effect of various parameters can be illustrated. The site dimensions are 18 meters long, 12 meters wide and 1 meter thick, with constant porosity of 30%. Longitudinal and transverse dispersivity are 0.1 cm and 0.01 cm, respectively. Geological heterogeneity is accounted for by means of stochastic permeability fields (Goff and Jennings, 1997). Input for these realizations includes the mean, the variogram type, the scale factors in the corresponding directions and a random number seed. The base case realization was generated using the following parameters:

Seed	1
Variogram model	Exponential model
Scale factors in x, y and z direction	$\gamma_x=1, \gamma_y=1, \gamma_z=1$
Average logarithm permeability	$\log k = 1$ Darcy
Standard deviation of log permeability	$Sdv \log k = 1$ Darcy

The exponential variogram mode used in this work is $\gamma(h) = S(1 - \exp(-(h/a)))$, where a is the scale factor, S is the sill (assumed to be unity in this work), and h is the lag distance.

The domain is discretized into 16x16x8 grid blocks. More refined grids (32x32x16 and 64x64x32) were used and showed no qualitative differences in terms of the effects of the parameters being studied, and thus for convenience the results presented here will be for the coarse grid.

The NAPL contaminant source is assumed to be a mixture of trichloroethylene (TCE) and perchloroethylene (PCE) in a molar ratio of 0.725 : 0.275. The overall NAPL solubility in water is $K =$

0.00631M, and the NAPL dissolution rate constant is assumed to be $k_{\text{diss}} = 0.1 \text{ min}^{-1}$. The initial concentration of the NAPL phase is $C_{\text{imm}} = 0.1$ mole per liter pore volume, corresponding to a volume fraction of 0.009. The NAPL phase was confined to a roughly triangular region in the bottom 0.5 m of the site, Fig. 1.

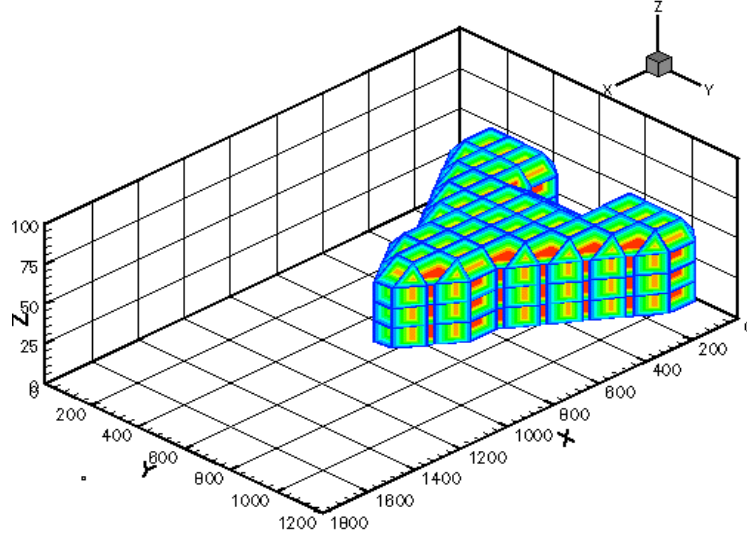
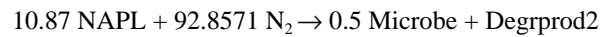
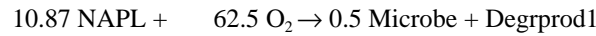


Figure 1. Initial distribution of the NAPL phase is confined to the bottom half of the aquifer in a roughly triangular region. Background flow is in the positive X direction.

There is no microbial activity in the base case. To examine the effects of biodegradation, active microbes are assumed to be uniformly distributed in the field and immovable. Injected water is assumed saturated with electron acceptors oxygen and nitrogen. Biodegradation occurs with the following molar stoichiometry:



The other parameters for the biodegradation reactions are listed below:

Component	H_i	k_{EA}	Initial Conc.	Injected Conc.
Oxygen	$3.125 \times 10^{-6} \text{M}$	10 min^{-1}	0	$2.643 \times 10^{-4} \text{M}$
Nitrogen	$9.2857 \times 10^{-5} \text{M}$	10 min^{-1}	0	$5.153 \times 10^{-4} \text{M}$
Dissolved NAPL	$1.8913 \times 10^{-4} \text{M}$	--	0	0
Microbe	--	--	0.216M	--

Three injection wells are located in a line at the rear of the NAPL zone, with an extraction well downstream and offset from the centerline of the NAPL zone, shown in plan view in Fig. 2. Each injection

well takes 11.7 m³/d, and the extraction well is operated at 35 m³/d so as to balance the injection. The wells are completed only in the bottom half of the site, in the same layers in which the NAPL exists. These rates give a nominal residence time of 1.9 days in the aquifer. A background natural flow is imposed in the positive X direction through the site. This flow is negligible in comparison to the injection/extraction rates. The injection is assumed not to disrupt the background hydraulic gradient, however, so that no injected fluid exits through the domain boundary at X=0. The Y and Z faces of the domain are no-flow boundaries.

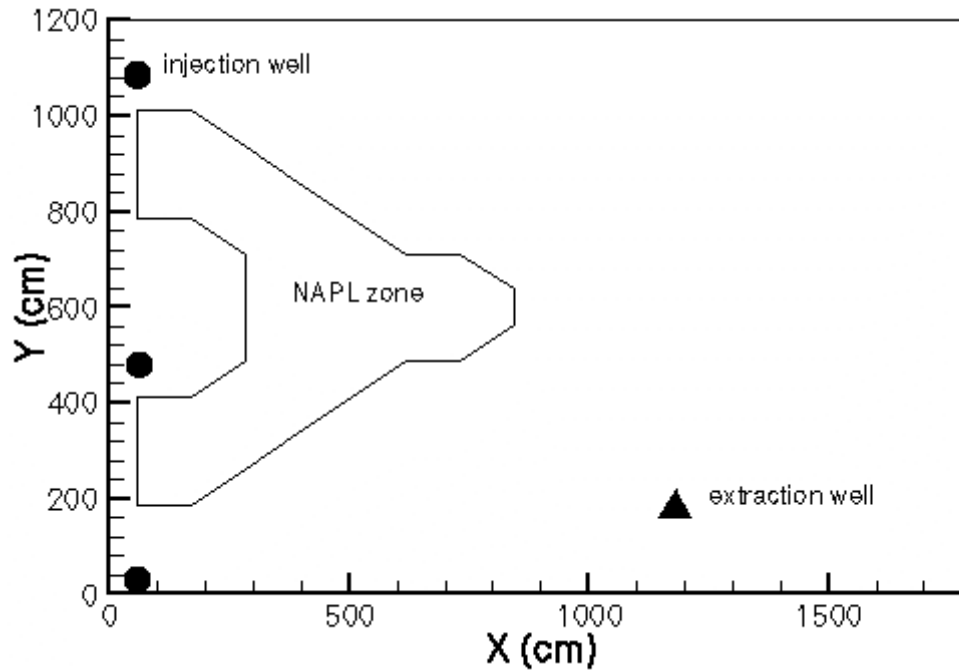


Figure 2. Plan view of well locations and NAPL source.

Evaluation of Influence of Physicochemical Parameters

In this work the measure of the extent of contamination and the result of remediation is the NAPL concentration at the extraction well. This concentration is calculated as a bulk-mixing average over the grid blocks penetrated by the well: $C = \Sigma(C_i Q_i)/Q$, where C_i is the dissolved NAPL concentration in grid block i , Q is the total production rate, and Q_i is the production rate from grid block i . Plots of C vs. time will illustrate the influence of the various physical and chemical parameters on the performance of the remediation process.

RESULTS

We first examine the effects of NAPL dissolution rate and well injection/extraction rates in the absence of biodegradation. The base case rate constant for NAPL dissolution is $k_{\text{diss}} = 0.1 \text{ min}^{-1}$. For the base case injection/extraction rate this yields a relatively fast dissolution rate, as becomes apparent when compared to the equilibrium limit. When the NAPL dissolution reaction is assumed to satisfy local equilibrium, the peak concentration of dissolved NAPL at the extraction well is only 25% higher than in the base case, Fig. 3. Within the source zone, aqueous concentrations reach the equilibrium value of 0.0063 M, but the peak concentration found at the extraction well is considerably below the equilibrium concentration. This is because of dispersion and because some injected fluid flows above and around the NAPL source zone, diluting the NAPL-loaded fluid that has passed through the source zone. This demonstrates that field observations of sub-equilibrium concentrations are not necessarily indicative of non-equilibrium conditions. If the base case value of k_{diss} is reduced by a factor of ten, the peak concentration is much lower, and a long tail is observed as the NAPL source slowly dissolves away.

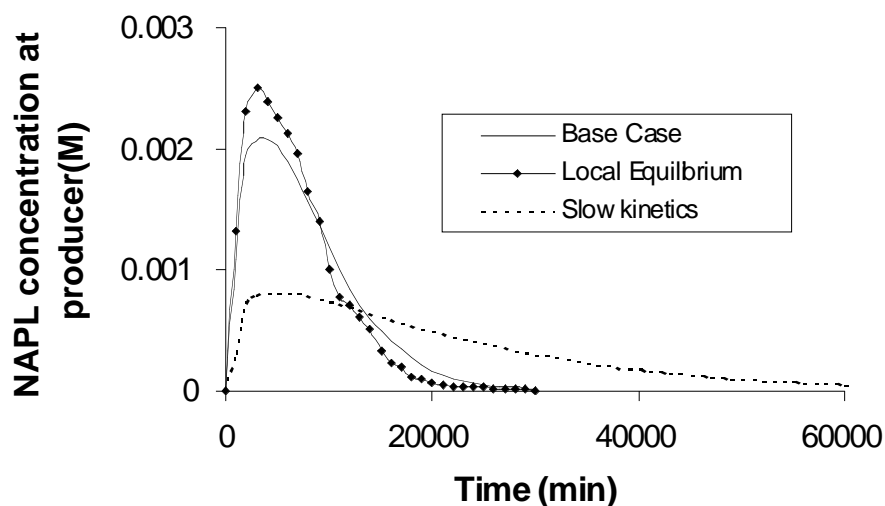


Figure 3. In the absence of biodegradation, the peak concentration of dissolved NAPL at the extraction well is highest when the dissolution reaction goes to equilibrium. As the rate of dissolution decreases, the peak concentration declines, but the concentration reaching the well at later time increases.

The effect of well injection rate is closely related to the effect of NAPL dissolution rate, although they are not interchangeable because of the velocity dependence of dispersion. Slower injection rates yield

higher dissolved NAPL concentrations at the extraction well, Fig. 4, since the residence time in the NAPL zone increases. At the lowest rate tested, the NAPL concentration history approaches the local equilibrium limit; compare Figs. 3 and 4. The variation of injection rate introduces a tradeoff between the volume of fluid required to achieve a given level of remediation and the time required to reach that level. The lower flow rates are more efficient in that less fluid must be processed, Fig. 4, but for the cases tested require significantly longer, Fig. 5.

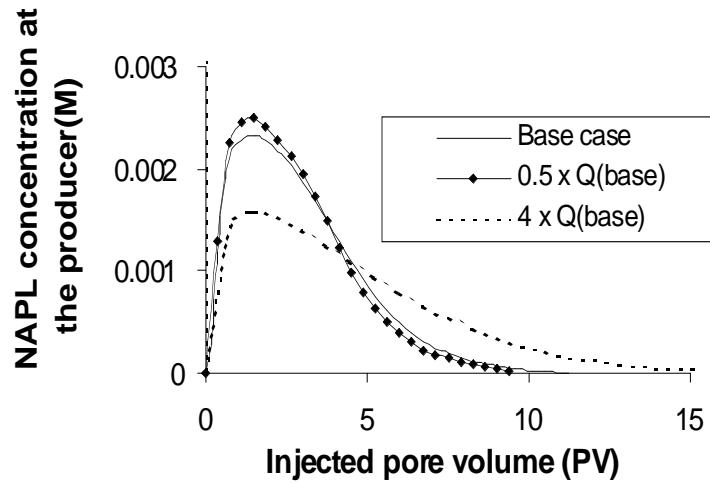


Figure 4. Increasing the flow rate reduces the efficiency of the injected fluid for dissolving NAPL, so that more pore volumes are required to reach the same dissolved NAPL concentration.

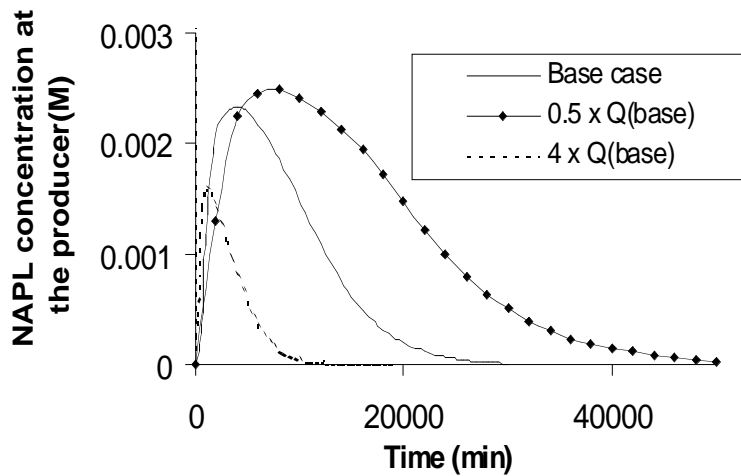


Figure 5. Although higher injection rates require larger volumes of fluid to reach the same dissolved NAPL concentration at the extraction well, Fig. 4, the higher rates also mean that less time is required. Thus tradeoff arises between handling larger volumes of fluid and carrying out the remediation process for longer times.

Let us now consider the influence of biodegradation by in-situ microbes. For the operating conditions of the base case biodegradation has little effect during the early part of the process. This is because the O_2 and N_2 in the injected water are sufficient to degrade only a small fraction of the NAPL that dissolves into the water. As the NAPL source disappears, the rate of dissolution decreases, and the effect of biodegradation becomes important. This occurs at about 20000 min in the base case of relatively fast NAPL dissolution, Fig. 6. If the rate of dissolution is an order of magnitude slower, the biodegradation reactions dominate the behavior from the outset, Fig. 6. This is an important to consider when evaluating field results. If biodegradation is significant, the concentration of contaminant reaching an extraction or monitoring well may fall below targeted levels even though large amounts of NAPL phase remain in place in the source zone. If injection of water saturated with oxygen and nitrogen were halted, however, high levels of contamination could return. The slower flow rates of the natural hydraulic system would increase the residence time of fluid in the NAPL zone, and if the natural waters are undersaturated with respect to oxygen and nitrogen, much higher concentrations of NAPL could arise.

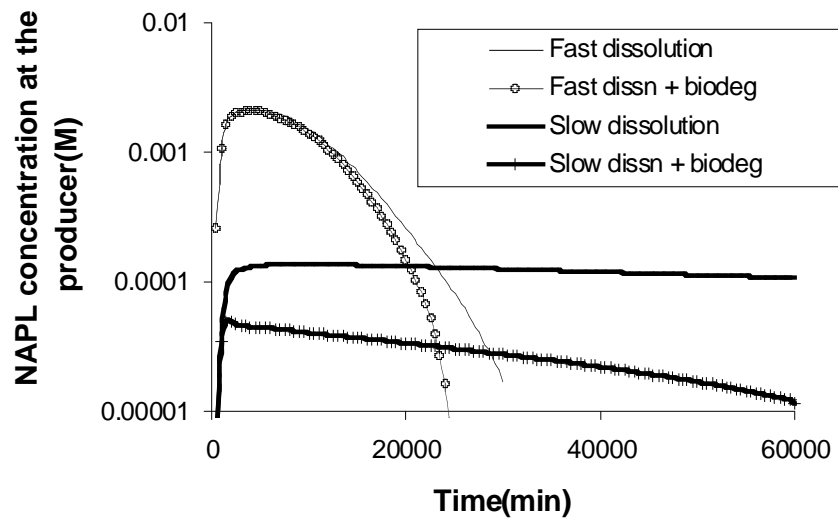


Figure 6. The influence of biodegradation depends on the relative rate of dissolution. In a dissolution-dominated regime, biodegradation may not even be apparent until late in the remediation process. If dissolution is sufficiently slow, biodegradation can significantly reduce observed dissolved NAPL concentrations, even when the contamination source remains largely intact.

The heterogeneity of the permeability field influences flow paths and hence local residence time for mass transfer and reaction. Figures 7 and 8 compare the behavior of the base case to that of a homogeneous aquifer (uniform permeability equal to the arithmetic average permeability of the heterogeneous field). The distribution of streamlines in the heterogeneous field has more fast and more slow paths, resulting in a higher peak concentration that arrives earlier, as well as a longer tail. The tail is clearly evident when concentration is plotted on a logarithmic scale, Fig. 8. Increasing the heterogeneity of the permeability field, in this case by doubling the standard deviation of the frequency distribution underlying the permeability realization, increases the peak and extends the tail still further.

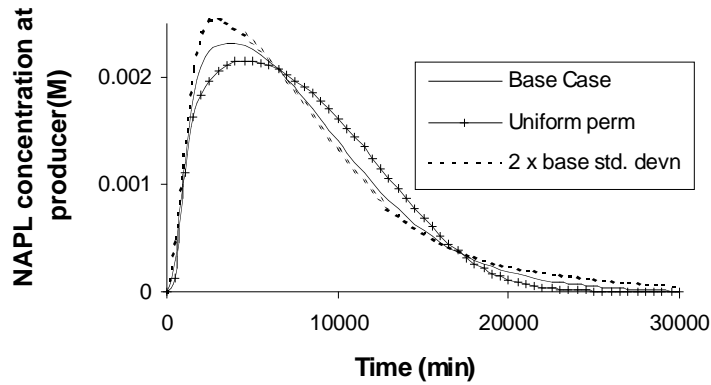


Figure 7. Heterogeneity causes a larger peak concentration of dissolved NAPL to arrive at the extraction well. A longer tail also occurs, seen more clearly in Fig. 8.

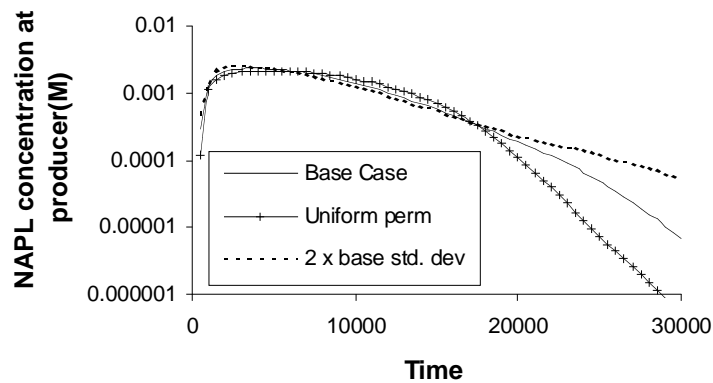


Figure 8. Heterogeneity causes a longer tail in the concentration of dissolved NAPL reaching the extraction well.

The base case operating conditions are at high Peclet number, and changing longitudinal dispersivity does not have a large effect. In contrast, increasing transverse dispersivity has a significant effect. This is because flow is primarily in the X direction, and a dispersive flux transverse to this direction allows dissolved NAPL to move into the upper part of aquifer. This flux in effect increases the dissolution rate in the NAPL zone. Consequently higher concentrations of dissolved NAPL reach the extraction well early in the pump-and-treat process. This contrasts with the usual effect of dispersion, which is to reduce concentration gradients. Johnson and Pankov (1992) and Anderson et al. (1992) have also noted the importance of transverse dispersion for persistence of NAPL sources. Because more NAPL is dissolved in the early part of the process, the high transverse dispersion case exhibits a smaller tail in the NAPL concentration history.

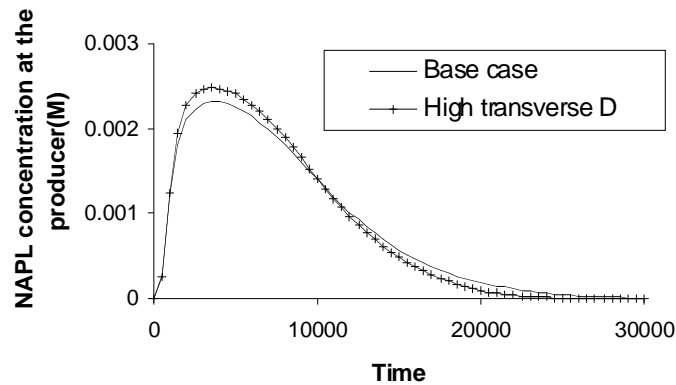


Figure 9. Increasing transverse dispersion has the counterintuitive effect of increasing the concentration of dissolved NAPL reaching the extraction well. This arises because the dispersion induces a flux into the region above the NAPL source, effectively increasing the rate of dissolution.

DISCUSSION

Let us return to the situation in which observed NAPL concentrations at a monitoring well are higher than expected based on previous simulations. From the preceding discussion it is apparent that the model could be adjusted to account for the discrepancy by increasing the dissolution rate constant, decreasing the degradation rate, increasing transverse dispersivity, or increasing the heterogeneity of the permeability field. Other parameters not discussed here could also be changed, such as microbe concentration or distribution. Each of these parameter adjustments may have different long-term

implications for the performance of the remediation process. In this case, increasing the transverse dispersivity or increasing the dissolution rate will result in a smaller NAPL tail later in the process, whereas increasing the heterogeneity or decreasing the biodegradation rate will have the opposite effect. Thus it is important to understand all factors that may be relevant in a particular process and to eliminate as many as possible from consideration. This highlights the utility of obtaining additional data whenever feasible, such as tracer data to enable better characterization of dispersion and heterogeneity. It is difficult to obtain a reliable understanding of a process from a single snapshot, since even in as simple a system as those illustrated here, a different process may dominate behavior at different times.

CONCLUSIONS

NAPL contamination of groundwater and its remediation are the result of complex interplay between fluid residence time in the subsurface and rates of mass transfer and reaction. Thus physical factors that influence fluid residence time, such as heterogeneity of the permeability field and well injection/extraction rates, are coupled to rates of NAPL dissolution and biodegradation. Mechanical factors such as dispersion can enhance mass transfer as well as attenuate contamination, depending on the flow field and the location of the contaminant source. The coupling between these factors can make interpretation of field data difficult. For example, NAPL dissolution may approach local equilibrium, yet concentrations considerably below the solubility limit can be observed downstream of the contaminant source. Relatively rapid dissolution may mask the activity of in-situ microbes early in a process, leading to unduly pessimistic predictions of long-term behavior. Conversely, the combination of biodegradation with relatively slow dissolution can lead to unduly optimistic predictions of treatment duration, since low levels of contaminant may be found downstream despite a large remaining mass of NAPL phase.

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