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Transport issues and bioremediation modeling for the *in situ* aerobic co-metabolism of chlorinated solvents

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Abstract

For aerobic co-metabolism of chlorinated solvents to occur, it is necessary that oxygen, a primary substrate, and the chlorinated compound all be available to an appropriate microorganism – that is, a microorganism capable of producing the nonspecific enzyme that will promote degradation of the contaminant while the primary substrate is aerobically metabolized. Thus, the transport processes that serve to mix the reactants are crucial in determining the rate and extent of biodegradation, particularly when considering *in situ* biodegradation. These transport processes intersect, at a range of scales, with the biochemical reactions. This paper reviews how the important processes contributing to aerobic co-metabolism of chlorinated solvents at different scales can be integrated into mathematical models. The application of these models to field-scale bioremediation is critically examined. It is demonstrated that modeling can be a useful tool in gaining insight into the physical, chemical, and biological processes relevant to aerobic co-metabolism, designing aerobic co-metabolic bioremediation systems, and predicting system performance. Research needs are identified that primarily relate to gaps in our current knowledge of inter-scale interactions.

Introduction

As has been discussed in accompanying papers in this issue (Arp & Hyman, 2000; Alvarez-Cohen & Speitel, 2000), aerobic co-metabolic bioremediation is dependent on a primary substrate (the electron donor), dissolved oxygen (the electron acceptor), nutrients, a contaminant, and microorganisms being brought together. The microorganism, in the presence of the electron donor and acceptor, is induced to produce a nonspecific enzyme that will fortuitously promote degradation of the contaminant. Subsurface transport processes that serve to bring together microorganism, electron donor, acceptor, and contaminant, thus play a crucial role in determining the rate and extent of contaminant co-metabolism. These processes occur over scales that range from the microbial cell and the hydrodynamic boundary layer (μm) to the scale of the site (10–1000 s of meters) (Sturman et al., 1995). The lack of methods to efficiently mix contaminant, microorganisms, electron donors and acceptors must be considered as perhaps the most significant engineering limitation in implementing *in situ* bioremediation (McCarty & Semprini, 1993).

Aerobic co-metabolism of chlorinated solvents in the field involves complex interactions of the physical transport processes discussed above, occurring over a wide range of scales, with biological and chemical processes that occur at relatively small scales. Due to the complexity of these interactions, the variety of phenomena involved, and the range of scales being considered, modeling is the most effective approach to gaining understanding of relevant processes, designing bioremediation systems, and predicting system performance. In particular, models may be crucial in convincing regulators, site owners, and the public of the relative benefits of implementing aerobic co-

metabolic bioremediation to remediate a chlorinated solvent contaminated site (McCarty et al., 1998).

The purpose of this article is to review how the important processes contributing to aerobic co-metabolism of chlorinated solvents at different scales can be integrated into one or more mathematical models. The application of these models to field-scale bioremediation is critically examined. Research needs are identified that primarily relate to significant gaps or inadequacies in our current knowledge of inter-scale interactions.

Background

A general partial differential equation describing advective/dispersive transport in the subsurface, modified to include sorption, filtration of microorganisms, and biotransformation is (e.g., Javandel et al., 1984; Fetter, 1992):

$$\frac{\partial C}{\partial t} = \nabla\cdot(\tilde{D}\nabla C - \nu C) - \frac{\rho_b}{\epsilon}\frac{\partial S}{\partial t} - R_{\text{filt}} - R_{\text{bio}} - R_{\text{micro}}, \quad (1)$$

where C = concentration (of solute or microorganism) in aqueous phase (ML^{-3}); t = time (T); $\tilde{D}$ = dispersion tensor (L^2T^{-1}); S = sorbed mass of solute per mass of aquifer solid (-); ρ_b = bulk density of aquifer solids (ML^{-3}); ϵ = porosity of aquifer material (-); R_{bio} = rate of biotransformation of solute ($ML^{-3}T^{-1}$); R_{filt} = rate of filtration of microorganisms ($ML^{-3}T^{-1}$); R_{micro} = net rate of microbial growth ($ML^{-3}T^{-1}$), and the average pore water velocity vector (ν) in Equation (1) is determined by Darcy's Law:

$$\nu = \frac{-K}{\epsilon}\text{grad}(h), \quad (2)$$

where K = hydraulic conductivity tensor (LT^{-1}); h = hydraulic head (L).

Equations (1) and (2) are general, and may be used to describe groundwater transport of dissolved contaminant, electron donor, electron acceptor, nutrient, or microorganisms. The $(\rho_b/\epsilon)(\partial S/\partial t)$ and R_{bio} terms apply to solute transport, whereas the R_{filt} and R_{micro} terms apply to microbial transport.

In order to gain a better understanding of the impact of transport processes on aerobic co-metabolism, it is useful to define scales of observation. Following Sturman et al. (1995), we define the microscale as the scale at which chemical and microbiological phenomena may be characterized independent of transport (physical dimension $\sim 10^{-6} - 10^{-5}$ m). The fourth (R_{bio}) and fifth (R_{micro}) terms on the right hand side of Equation (1) are source/sink terms representing transformations that occur at the microscale. Sturman et al. (1995) define the mesoscale as the scale at which transport phenomena and system geometry become first apparent (physical dimension $\sim 10^{-5} - 10^{-2}$ m). The second $(\rho_b/\epsilon)(\partial S/\partial t)$ and third (R_{filt}) terms on the right hand side of Equation (1) represent sorption of solutes and filtration of microorganisms, phenomena which occur at the mesoscale. Finally, the first term on the right hand side of Equation (1) represents advection and dispersion, which are macroscale phenomena (physical dimension $> 10^{-2}$ m). Figure 1 illustrates these scales, and the relevant processes associated with each of them.

Review of topic

Using the above definitions of scale as a guide, the following sections examine how transport processes, acting at different scales, impact aerobic co-metabolic bioremediation of chlorinated solvents. The subsequent discussion addresses how models may be used to integrate the processes occurring at different scales to analyze the potential for *in situ* bioremediation in the field, to gain understanding for proper system design, and to predict system performance.

Macroscale

Advection/dispersion

Advection refers to transport due to the motion of the flowing groundwater while dispersion is a mixing phenomenon, where water with a solute is mixed with water without the solute, thereby reducing the concentration of the solute and spreading the zone of contamination. Dispersion is caused by molecular diffusion (at the micro and mesoscales), differences in velocity as water flows through intergranular pore spaces (at the mesoscale), and differences in flow rate as water passes through geological strata with differing hydraulic conductivities (at the macroscale). As dispersion due to hydraulic conductivity heterogeneity typically dominates field-scale transport (unless the aquifer is exceptionally homogeneous or the scale of interest is very small), the following discussion will focus on this macroscale phenomenon.

The enhancement of *in situ* aerobic co-metabolism of chlorinated solvents often involves the addition of

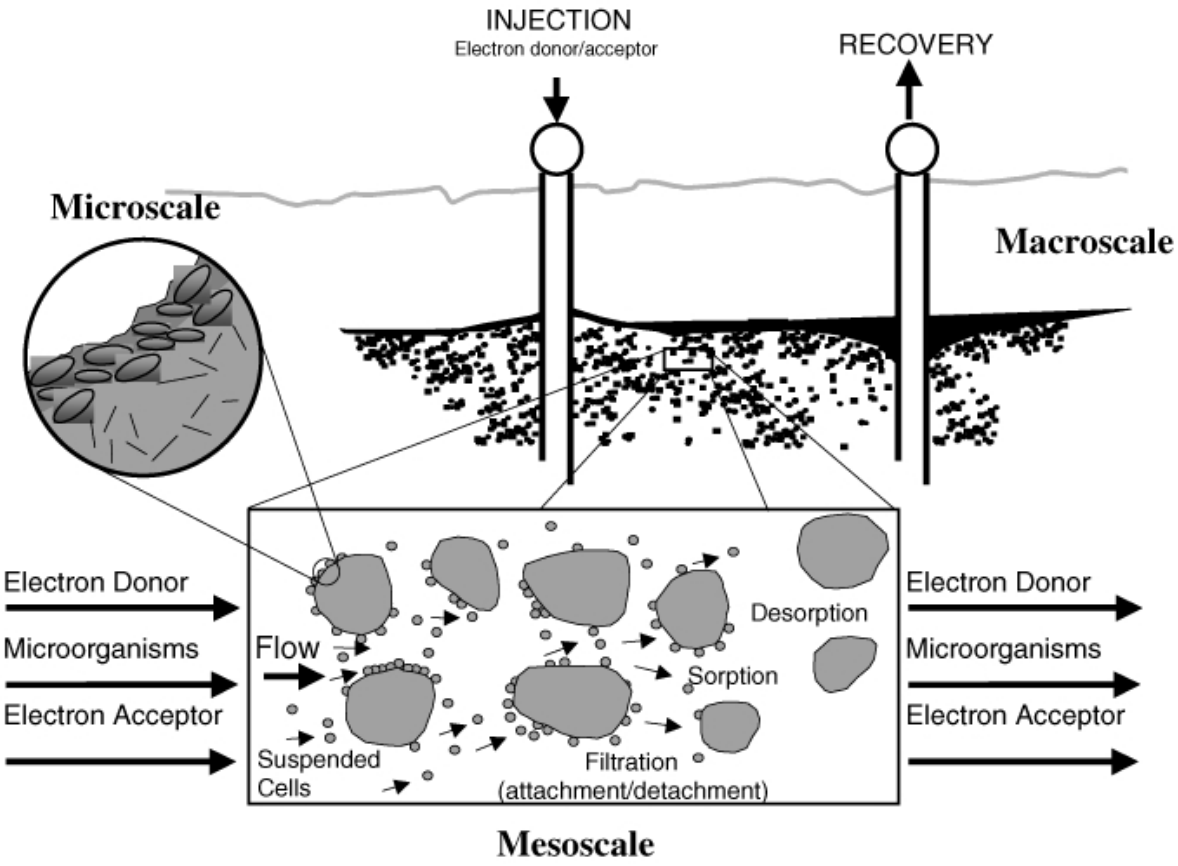

Figure 1. Scales of observation pertinent to *in situ* bioremediation (after Sturman et al., 1995).

electron donors and oxygen. Since groundwater flow is essentially laminar flow, the absence of turbulent conditions in the subsurface means that little mixing occurs when a chemical is injected into an aquifer. The limited mixing during simple injection of a chemical means that only a narrow portion of a contaminant plume can be treated, thereby diminishing the usefulness of an engineered *in situ* approach. As noted earlier, one of the most crucial requirements in implementing *in situ* bioremediation is having the ability to efficiently mix contaminant, microorganisms, electron donors and acceptors (McCarty & Semprini, 1993). Lang (1995) reviewed methods that have been used to promote mixing (macroscale dispersion). A common strategy, the injection of electron donor and acceptor enriched water into contaminated groundwater, is problematic because, due to advection, groundwater containing the contaminants will be displaced by the injected water. Mixing of contaminant and electron donor/acceptor will be limited to the zone around the edges of the injected water where the injected water and the contaminant plume mix due to dispersion (Figure 2). In an attempt to overcome this problem and promote mixing, various schemes have been proposed and implemented to inject donor/acceptor into recirculating groundwater. Recirculation may be established by an injection/extraction two-well system (McCarty et al., 1991), by a dual-screened single-well system (Herrling et al., 1991; Semprini et al., 1992), or by a pair of dual-screened wells (McCarty et al., 1998).

The consequences of dispersion have been exploited by bioremediation system designers to control mixing of the primary substrate with the electron acceptor and contaminant. Since the presence of primary substrate competitively inhibits contaminant co-metabolism (Arp & Hyman, 2000), it is disadvantageous to continually inject primary substrate into contaminated groundwater. To deal with this problem, investigators attempting to implement aerobic co-metabolism in the field have injected short pulses

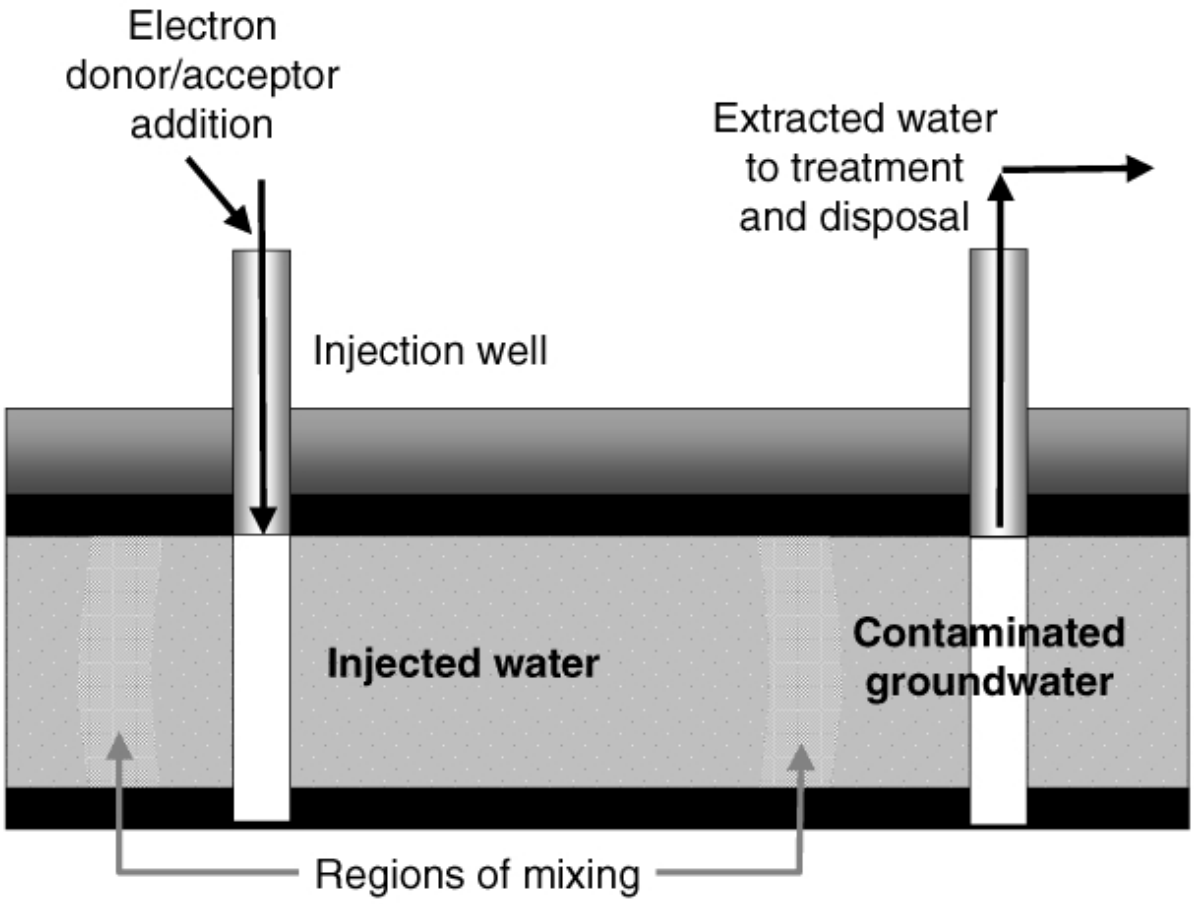

Figure 2. Mixing of electron donor/acceptor and contaminant using an injection and extraction well (after Lang, 1995).

of primary substrate at high concentration (Hopkins & McCarty, 1995; McCarty et al., 1998) while continuously injecting electron acceptor. Since the primary substrate, electron acceptor, and contaminant are only present simultaneously for a short time (the duration of the pulse), competitive inhibition is minimized. As the primary substrate pulse moves through the aquifer, it spreads due to dispersion, mixing with the electron acceptor and contaminant and undergoes a gradual reduction in concentration. Thus, primary substrate is supplied to microorganisms far from the injection well. Using a strategy of continuous injection of electron donor and acceptor, which doesn't rely on dispersive mixing, these outerlying microorganisms might never be supplied with primary substrate, as the substrate would be consumed by organisms close to the well. Pulsing thus has the added advantage of slowing microbial growth close to the well, thereby reducing the potential for clogging (i.e., biofouling). Figure 3 shows model simulations of two bioremediation systems, one with pulsed pumping of primary substrates, the other with continuous addition of substrate. Although the time-averaged concentration of substrate added is the same for both systems, Figure 3 shows that the contaminant concentrations measured at a downgradient well are lower for the pulsed system than for the continuous system. Figure 4 shows that the microbial growth in the continuous system is closer to the injection well and at higher concentration than for the pulsed system, so that biofouling might be a concern.

Figures 3 through 5 depict the impact of the primary substrate pulsing schedule on bioremediation. The numerical model used to create the figures combines a three-dimensional steady-state groundwater flow model with a transport model that includes advection, dispersion, equilibrium or rate-limited sorption, and co-metabolic biodegradation and microbial

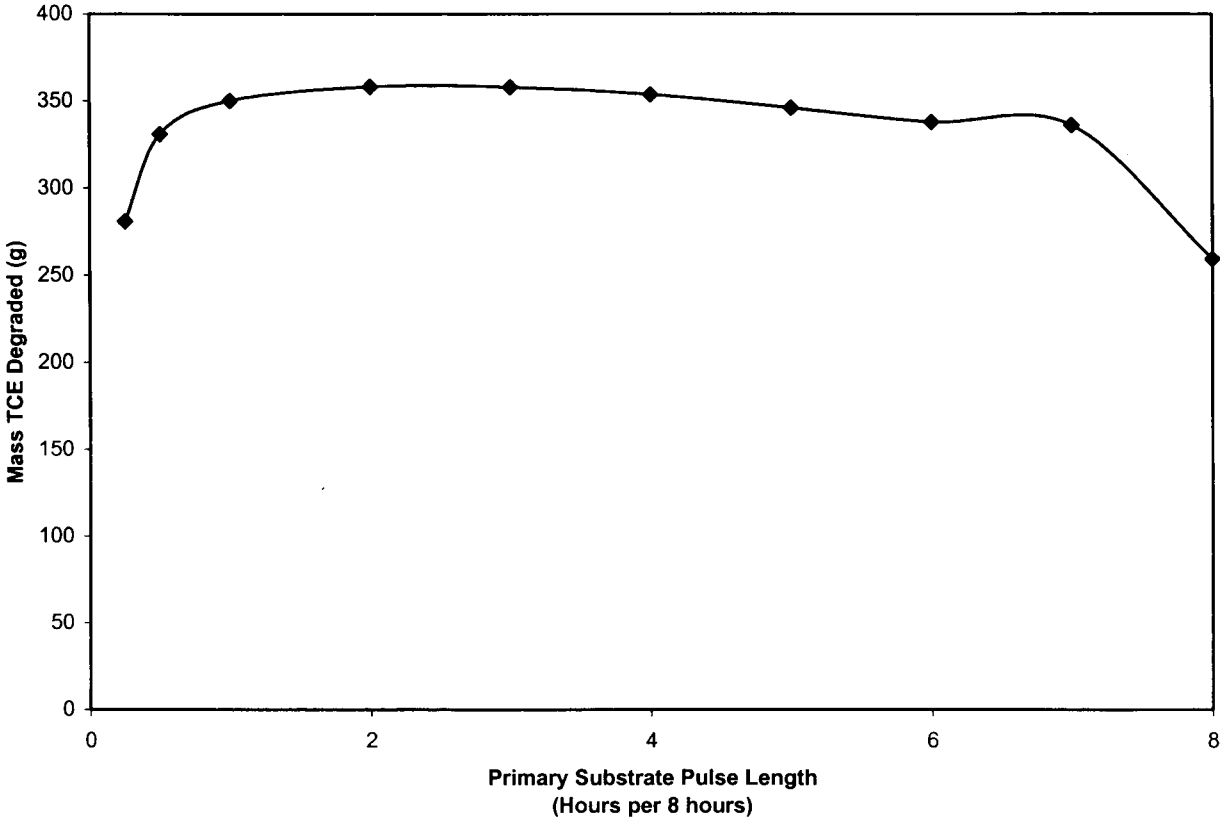

Figure 3. Degraded TCE mass after 200 days of operation vs. primary substrate pulse length (time-averaged primary substrate concentration = 8.5 mg/L).

growth kinetics. The submodel used to describe the microscale co-metabolic biodegradation and microbial growth processes is after Semprini and McCarty (1992). The submodel incorporates dual-Monod kinetics, competitive inhibition, and microbial deactivation (see Table 1). The scenario modeled is based on the full-scale evaluation of *in situ* aerobic cometabolic bioremediation at Edwards AFB (McCarty et al., 1998), where two dual-screened biotreatment wells were used to capture and treat trichloroethylene (TCE) contaminated groundwater. Hydrogeological and system parameters used in the model were taken from McCarty et al. (1998), while microbiological parameters were based on typical values presented in Semprini & McCarty (1991, 1992) and Jenal-Wanner & McCarty (1997). In the figures, the time-averaged primary substrate concentration is the same for all primary substrate pulse times. At very short pulse times (corresponding to high actual primary substrate concentrations) the mass of TCE degraded over 200 days of operation is relatively low (Figure 3). The reason for this is shown in Figure 4. At very short pulse times, microbial growth near the well is minimal, since primary substrate is available to promote growth for only a very short period of time and during that period, the electron acceptor concentration is much lower than the primary substrate concentration. When such a pulsing strategy of very short pulses of high primary substrate concentration is applied, model simulations show that the concentration of primary substrate downgradient from the treatment system is significant (Figure 5). This may be of concern if a potentially hazardous primary substrate (e.g., toluene) is used. Figure 3 also shows that as the addition of primary substrate becomes nearly continuous (right-hand portion of the graph), contaminant mass degradation is also decreased, presumably due to competitive inhibition. Figure 4 shows that nearly continuous input of primary substrate also leads to high concentrations of microorganisms near the injection well, perhaps resulting in hydraulic conductivity reductions (i.e., bioclogging).

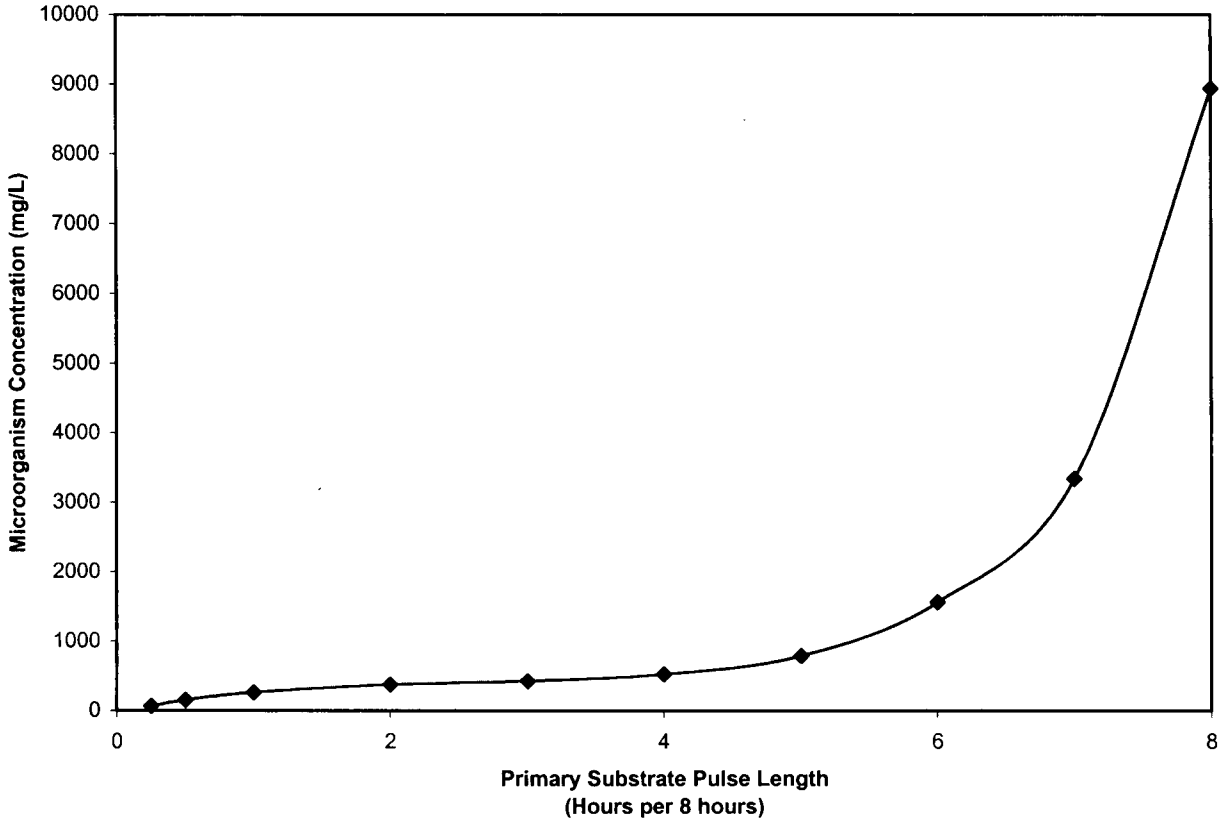

Figure 4. Microorganism concentration at the injection well after 200 days of operation vs. primary substrate pulse length (time-averaged primary substrate concentration = 8.5 mg/L).

Figures 3 through 5 also serve to demonstrate how models may be useful in designing bioremediation systems. The model used to develop Figures 3 through 5 incorporates macroscale advection and dispersion, in three-dimensions, and microscale phenomena accounting for microbial growth and decay, and contaminant co-metabolic kinetics (including the effect of competitive inhibition). Not accounted for in the model are reductions in hydraulic conductivity that may accompany microbial growth. The results in Figure 4 suggest this may be an important process to incorporate into a future version of the model. The model results clearly demonstrate the efficacy of a pulsing strategy, and the relative insensitivity of mass degradation to primary substrate pulsing times, outcomes that may not have been apparent without conducting the modeling effort. The results depicted in Figure 5 indicate that after an initial startup period, downgradient concentrations of primary substrate are minimal. However, the model also shows that after months of operation, primary substrate concentrations may rise. This may be problematic, especially if the primary substrate is a potentially hazardous substance. The model results in Figure 5 may be useful in helping to design monitoring strategies (for example, in this case, long-term monitoring for primary substrate downgradient appears to be essential, even though short-term monitoring may indicate complete degradation of the primary substrate).

Mesoscale

Bioavailability (sorption/desorption and dissolution)

Field bioremediation rates may be limited by the availability of one of the necessary constituents for biotransformation: co-substrate, contaminant, electron acceptor, nutrients, or microorganisms capable of degrading the target compound. Since chlorinated solvents do not tend to sorb to subsurface materials as readily as many other hydrophobic hazardous chemicals (e.g., PAHs, PCBs, and pesticides) (Bedient et al., 1994), kinetic models for *in situ* aerobic co-metabolism of chlorinated solvents are generally

Table 1. Attributes of models which couple advective/dispersive transport with aerobic co-metabolism

Reference	Macroscale	Mesoscale	Microscale
Kindred & Celia (1989)	1. 1-D advection/dispersion 2. Homogeneous	1. Equilibrium sorption 2. Immobile bacteria	1. Monod kinetics
Semprini & McCarty (1992)	1. 1-D advection/dispersion 2. Homogeneous	1. Equilibrium and first-order sorption kinetics 2. Immobile bacteria	1. Dual Monod kinetics 2. Competitive inhibition 3. Microbial deactivation
Tompson et al. (1994)	1. 1-D advection/dispersion 2. Homogeneous	1. No sorption 2. Immobile bacteria	1. Monod Kinetics (resting state) 2. Microbial deactivation
De Blanc et al. (1996)	1. 3-D advection/dispersion 2. Homogeneous	1. Equilibrium sorption 2. Mobile and immobile bacteria 3. Equilibrium and first-roder partitioning between dissolved and separate phase contaminant	1. Triple Monod kinetics 2. Competitive inhibition 3. Degradation product toxicity
Travis & Rosenberg (1997)	1. 3-D advection/dispersion 2. Vadose zone transport 3. Two-phase flow 4. Heterogeneous	1. Equilibrium and first-order sorption kinetics 2. Immobile bacteria	1. Triple Monod kinetics 2. Competitive inhibition 3. Degradation product toxicity 4. Protozoan predation
Lang et al. (1997); McCarty et al. (1998)	1. Pseudo 2-D advection/dispersion 2. Homogeneous	1. Equilibrium and First-order sorption kinetics 2. Immobile bacteria	1. Dual Monod kinetics 2. Competitive inhibition 3. Microbial deactivation
Oya et al. (1997)	1. 1-D advection/dispersion 2. Homogeneous	1. Equilibrium and first-order sorption kinetics 2. Mobile and immobile bacteria	1. Dual Monod kinetics 2. Competitive inhibition 3. Degradation product toxicity

developed for the co-substrate and contaminant as limiting constituents (see paper by Alvarez-Cohen & Speitel, 2000). However, the influence of sorption in aquifers is sufficient to retard the rate at which chlorinated solvents move in groundwater relative to the rate of groundwater movement (Ball et al., 1997a). In situations where hydrophobic compounds are exposed to sediments for long periods, the rate and extent of biodegradation can be limited by sorption and reduced bioavailability (Mihelcic et al., 1993; Zhang et al., 1998).

Prolonged exposure to subsurface solids allows hydrophobic compounds, such as chlorinated solvents, to sorb to intraparticle organic carbon. This sorption reduces the fraction of the compound in the bulk water. Over long contact time, the sorbing pollutants slowly diffuse into the inorganic and organic solid matrix and may also form bound residues. Most evidence indicates the uptake of compounds by bacteria proceeds via the liquid phase. Consequently, a process such as sorption or volatilization that reduces the solution concentration tends to reduce the biotransformation rate. Furthermore, the accumulation of contaminants in fissures and cavities within subsurface solids renders them inaccessible to microorganisms and their enzymes. These processes decrease the bioavailability.

The presence of chlorinated solvent contamination in heterogeneous subsurface environments also creates a bioavailability issue. The less-permeable strata (e.g., silt and clay aquitards) become contaminated during prolonged exposure to contaminated groundwater moving through the permeable strata (e.g., sands and gravels) (Ball et al., 1997b). Molecular diffusion is typically the dominant contaminant transport process controlling the contamination of the aquitards. Slow diffusion from the contaminated zones often becomes the limiting factor affecting biodegradation rates or the performance of other remedial technologies (e.g., pump and treat).

In systems where a pure organic phase (NAPL) is present, bioavailability will be controlled, in part, by the rate at which compounds dissolve from the NAPL. In locations where free NAPL is absent, sorptive processes may ultimately control bioavailability. The model described in this paper considers bioavailability through the coupling of sorption and biodegradation processes. The second term on the right hand side of Equation (1) accounts for sorption kinetics. Typ-

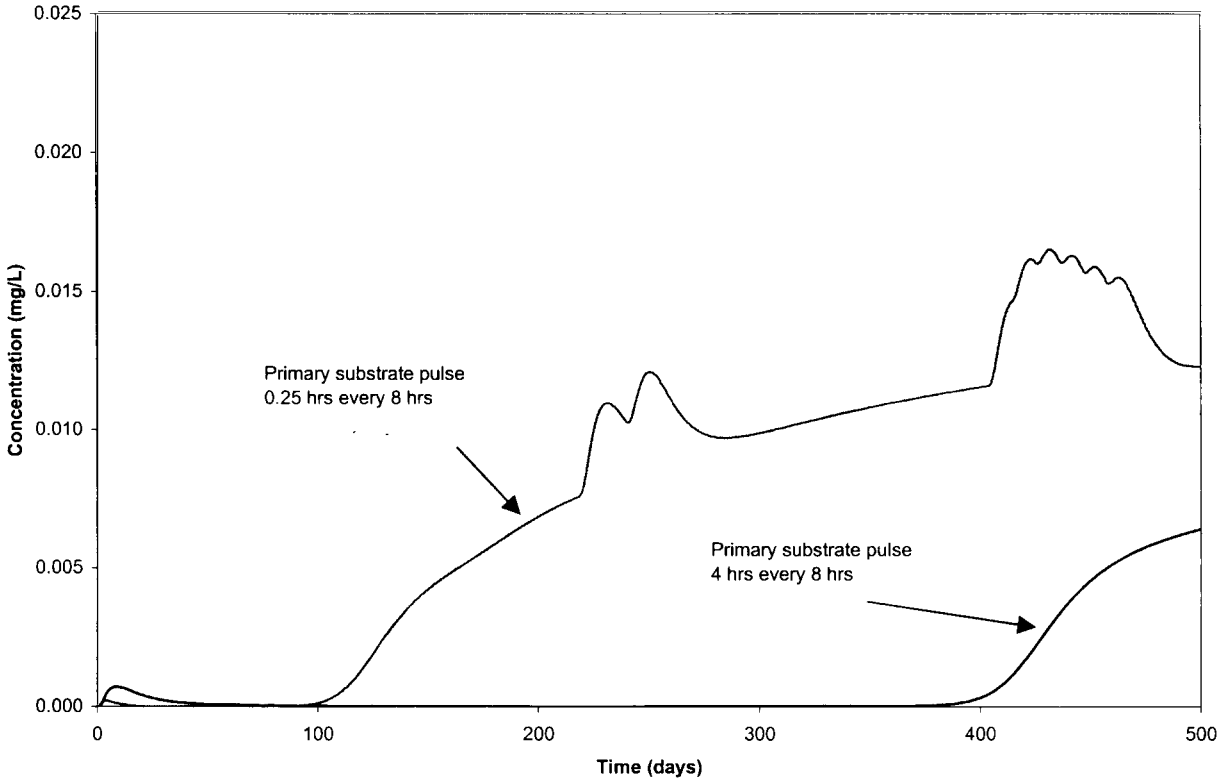

Figure 5. Primary substrate concentration at a downgradient monitoring well vs. time for two primary substrate pulsing strategies (time-averaged primary substrate concentration = 8.5 mg/L).

ically, sorption kinetics are described by a first-order rate expression or by Fick's law of diffusion. NAPL dissolution kinetics are also frequently described using a first-order rate expression. Thus, although the second term on the right hand side of equation (1) is specifically written for sorption, the same mathematical formulation may be used to describe dissolution of a NAPL.

The impact bioavailability can have on the operation of an aerobic chlorinated solvent bioremediation system is shown in Figure 6. The model and parameter values are the same as were used in Figures 3 through 5. Simulations are based on the conditions at the Edwards AFB test site (McCarty et al., 1998). Two groundwater circulation wells pump TCE contaminated water with no regional flow to simulate a pseudo-batch system. Toluene is injected in the wells as the primary substrate. TCE co-metabolism occurs in the bioactive zones that form around the injection screens of the two wells. Three scenarios are compared in Figure 6: (1) no sorption (100% bioavailability), (2) equilibrium sorption (instantaneous and completely reversible), and (3) rate limited sorption (least amount of bioavailable TCE; first-order sorption rate constant of 0.01/day). The greatest persistence of TCE (slowest bioremediation) occurs under the rate-limited case. The TCE degraded for the rate-limited case lags the equilibrium sorption case on the order of 100 days.

Additional insight into the influence of bioavailability on bioremediation is shown by the breakthrough response depicted in Figure 7. Figure 7, which uses the model and parameter values used to create Figures 3 through 5, compares two scenarios, one where equilibrium transport of contaminant is assumed, the other where desorption of sorbed contaminant (or alternatively, dissolution of contaminant in the NAPL phase) is rate-limited. Other than the rate of sorption, the two scenarios are identical. A first-order expression is used to represent mass transfer kinetics. Figure 7 shows that although sorption kinetics have a short-term impact on contaminant concentrations downgradient of the treatment system (earlier breakthrough and tailing), in the long-term, as the system approaches steady-state, downgradient concentrations

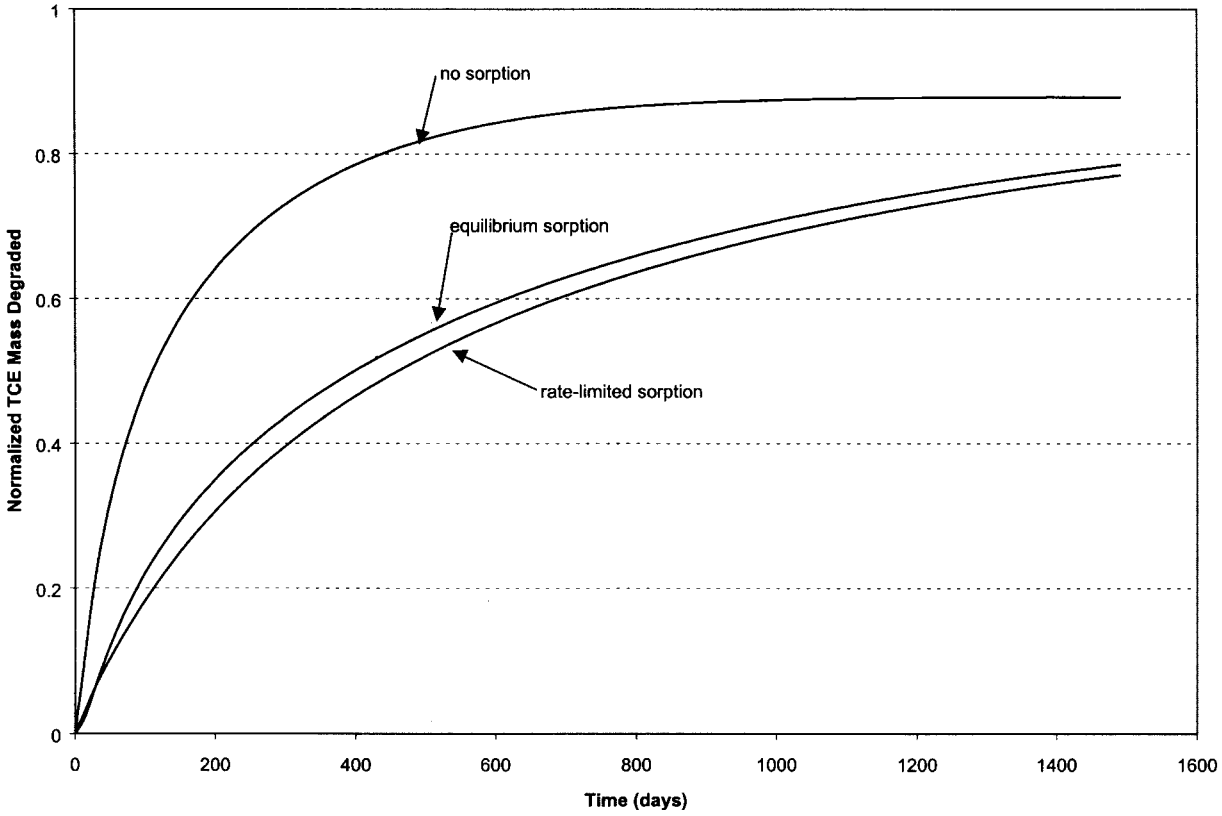

Figure 6. TCE degraded vs. time for pseudo-batch systems with no sorption, equilibrium sorption, and rate-limited sorption.

simulated by equilibrium and kinetic sorption models are the same.

Additional information on theoretical and experimental issues surrounding the influence of mass transfer rate on the overall biodegradation is presented elsewhere (Alexander, 1995; Bosma et al., 1997; Zhang et al., 1998).

Microbial transport

Modeling the dispersal of indigenous and introduced bacteria may be of interest for bioremediation. Such modeling has particular application if the appropriate, naturally occurring microbial populations are not present, and introduction of a variety of microbial strains carrying genes encoding the requisite metabolic pathways is attempted. At the mesoscale, filtration theory (Yao et al., 1971; Rajagopalan & Tien, 1976) has been widely used to model the transport of bacteria in porous media (Harvey & Garabedian, 1991; Gross et al., 1995; Martin et al., 1996). The rate of removal of bacteria due to filtration in porous media, that is, the R_{filt} term in Equation (1), is given by:

$$R_{\text{filt}} = -\frac{3}{2}\frac{(1-\epsilon)q}{d\epsilon}\alpha\eta C_{\text{microbe}}, \tag{3}$$

where ϵ = media porosity; α = collision efficiency; η = collection efficiency; q = superficial fluid velocity (L/T), C_{microbe} = concentration of microorganisms in the fluid phase (M/L^3) and d = collector or filter grain size (L). The value of η is typically calculated using the semiempirical expression of Rajagopolan & Tien (1976):

$$\eta = 4A_s^{1/3}N_{\text{Pe}}^{-2/3} + A_s N_{\text{Lo}}^{1/7} + 3.38\times10^{-3}A_s N_G^{1.2}N_R^{-0.4}, \tag{4}$$

where A_s = Happel's flow field factor = $2(1-p^5)/(2-3p+3p^5-2p^6)$, in which $p = (1-\epsilon)^{1/3}$; N_{Pe} = Peclet number = $6\pi\mu a_p q d/k_b T_a$, in which μ = fluid viscosity (M/LT), a_p = particle radius (L), k_b = Boltzmann constant (Joules/K), T_a = temperature (K); N_{Lo} = London group = $H/9\pi\mu a_p^2 q$, in which H = Hamaker constant (ML^2/T^2); N_R = relative size group = a_p/a_c, in which a_c = collector radius (L); and N_G = gravity group = $2a_p^2(\rho_p-\rho)g/9q$, in which ρ_p =

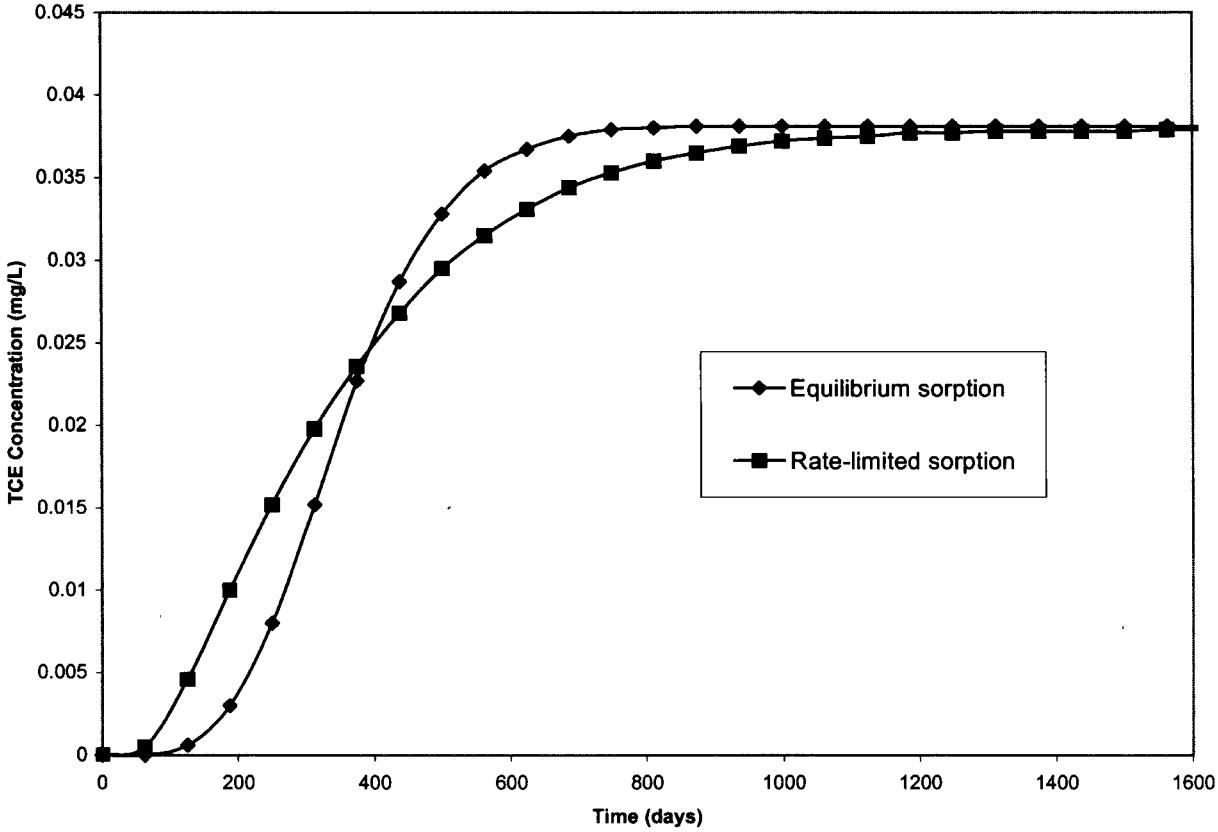

Figure 7. TCE concentration breakthrough at well downgradient of treatment system.

particle density (M/L^3), ρ = fluid density (M/L^3), and g = gravitational constant (L/T^2).

The collision efficiency α is defined as the rate bacteria stick to a soil grain to the rate they collide. The level of α is controlled by cell-solid interactions and by the amount of previously attached bacteria (Rijnaarts et al., 1996). The attached bacteria can reduce deposition by blocking a part of the collector surface. An expression for the collision efficiency that includes blocking becomes:

$$\alpha = \alpha_0(1 - B\theta), \tag{5}$$

where α_0 is the clean bed collision efficiency, B is the blocking factor, and θ is the fraction of surface covered.

Using parameters typical for subsurface systems, the filtration equation demonstrates that a major impediment to introduction of microorganisms is that the soil acts as an efficient filter and reduces the concentration of suspended bacteria by several orders of magnitude within 10 to 100 cm of the injection point if the α value is between 0.01 and 1.0 (Martin et al., 1996). The retention and growth of these bacteria over such a short distance can lead to clogging of the well and aquifer, ultimately causing failure of a bioremediation process.

Microscale

The solute transformation reactions accounted for by the fourth term (R_{bio}) on the right hand side of Equation (1), and microbial growth and decay accounted for by the fifth term (R_{micro}) occur at the microscale. Models characterizing these processes, as well as the interaction between solute consumption and microbial growth, have been described in detail elsewhere (e.g., Arp & Hyman, 2000; Alvarez-Cohen & Speitel, 2000), and will not be discussed here.

Process modeling

Several mathematical models have been proposed with application to *in situ* aerobic co-metabolism. The attributes of these models that couple advective/dispersive transport with co-metabolic biodegrad-

ation kinetics are listed in Table 1. The table describes the processes modeled at the micro-, meso-, and macroscales, which are integrated to simulate spatial and temporal patterns of contaminant distribution. As is apparent from the table, some of the more recent models incorporate more processes and complexity in both the transport (meso- and macroscale) and biodegradation (microscale) submodels.

McCarty et al. (1998) and Travis & Rosenberg (1997) used models in conjunction with two field evaluations of aerobic co-metabolic bioremediation of TCE at Edwards AFB and Savannah River, respectively. Let us look at how models were used to design and implement the field evaluations and aid in interpretation of the results.

When designing the dual-well field bioremediation system at Edwards AFB, McCarty et al. (1998) defined specific criteria to ensure that treatment effectiveness could be evaluated within time and cost constraints. The criteria they used were:

1. The direct flow path time from injection to extraction well should be 3–5 days.
2. After several months of operation, at least 80% of the water treated at the injection well should have arrived at the extraction well.
3. During several months of operation, TCE concentrations at the site should be demonstrably reduced.

Flow modeling was used to determine appropriate well spacing and pumping rates to ensure the first two criteria were met. The fate and transport model referenced in Table 1 (Lang et al., 1997; McCarty et al., 1998) was then applied to ensure the third criterion would be met for the conditions at the site and at specified schedules for injecting primary substrate and oxygen. Lang et al. (1997) used the fate and transport model to calculate optimal primary substrate and oxygen delivery schedules. Model simulations were also used to help assure site regulators that the proposed treatment system would eventually biodegrade the toluene primary substrate that was added, as well as capture and treat the TCE plume.

At the conclusion of the field evaluation, the same fate and transport model that had been used to design the experiment was used as an aid in interpreting results. The model simulations compared well with the measured concentrations downgradient of the treatment system (McCarty et al., 1998). Also, the measured response of concentration with time in the treatment zone near the injection wells was similar to the modeled response. These results provide confidence that the model captured the important processes (physical, chemical, and biological) that controlled contaminant fate and transport in the field. Of course, any modeling effort cannot hope to capture all relevant processes in a field situation or have appropriate values for all parameters, so further study is required. Discrepancies between model simulations and observations may have been due to model assumptions regarding homogeneity, steady flow, and problem two-dimensionality, which almost certainly do not accurately reflect reality. Also, important fate and transport processes may have been overlooked in the modeling. For example, clogging of the injection wells most likely from microbiological growth occurred periodically during the Edwards AFB demonstration. Although the fate and transport model applied to the site quantified the microbiological growth, the model did not account for the effects such growth might have on macroscale advective/dispersive transport.

Travis & Rosenberg (1997) developed a model to retrospectively interpret the data from the 1992–1993 demonstration of aerobic co-metabolic bioremediation at the Savannah River Site. In using the model to interpret demonstration results, the investigators were able to estimate difficult to measure quantities, such as total mass of TCE degraded. Also, by running "what if" simulations, for instance by turning off the biodegradation portion of the model but leaving the other fate and transport processes operative, the investigators could estimate the relative role biodegradation played in the total remediation. In addition, sensitivity analyses conducted using the model assisted in the identification of the controlling parameters and processes. A post-processor was used to present modeling simulation results in a format that simplified visualization and, therefore, aided in system conceptualization and interpretation. The authors conclude that their fate and transport model, particularly if coupled with an optimization code such as that used by Lang (1995), would be a very powerful tool in designing and operating a treatment system.

As with the Edwards AFB modeling efforts, model assumptions (for instance, assuming two-dimensionality and ignoring small scale heterogeneities) likely contributed to discrepancies between model simulations and field observations. Also, Travis and Rosenberg (1997) noted that the impact of predation by protozoa, which was modeled, is mathematically similar to the impact of competition between species of bacteria, which was not modeled. Such similarities may lead one to wrongly conclude from a model simulation that closely reproduces observations that one

process is important, when in fact, a totally different process is controlling. A similar observation was made by Nkedi-Kizza et al. (1984) who demonstrated that the rate of sorption to aquifer solids due to either physical or chemical processes could be mathematically described by identical formulations, so that the two processes could not be distinguished using modeling alone.

Knowledge gaps and research needs

The previous text has reviewed the role transport processes play in aerobic co-metabolic bioremediation of chlorinated solvents and has described the current approaches to modeling those processes. The section below addresses the knowledge gaps and research needs in the area of transport modeling as it relates to aerobic co-metabolism.

The understanding and quantitation of "intrascale" phenomena is fairly advanced. For example, there are numerous models that describe aspects of microscale biodegradation kinetics of co-metabolism (competitive inhibition, product toxicity, etc.) (Alvarez-Cohen & Speitel, 2000). Similarly, at the mesoscale and macroscale, modelers have relatively sophisticated descriptions of transport processes (advection/dispersion, sorption, bacterial attachment/detachment, etc.). Major knowledge gaps exist, however, at the interfaces between processes and scales. Submodels that incorporate the impact of bacterial growth on advective/dispersive transport have not been used in models of aerobic co-metabolism, though such submodels may provide insight into the potential for bioclogging at injection wells. The interactions between sorption and biodegradation phenomena is also not well understood or modeled, although such interactions can have significant impact on the efficacy of co-metabolic bioremediation. As discussed in the section on bioavailability, it is typically assumed that sorbed contaminant is not bioavailable, and that biodegradation and sorption act independently. Recently, however, it has been hypothesized that sorption/biodegradation may be coupled, with the presence of microbial cells serving to either enhance or suppress sorption/desorption processes (Voice et al., 1997).

Another area of needed study deals with microbial transport. Although models for microbial transport in porous media have been derived from particle filtration theories that have been in use for decades, microbial transport submodels have never been incorporated into a model describing co-metabolic bioremediation (see Table 1). Microbial transport is an important phenomenon to understand and model, especially if bioaugmentation is necessary to implement co-metabolism in the field (Tompson et al., 1994) and if microbial growth leads to clogging conditions.

The impact of heterogeneity on fate and transport during aerobic co-metabolic bioremediation is also deserving of further study. Although large-scale heterogeneities in hydraulic conductivity were modeled at the Savannah River Site, small-scale heterogeneities that could induce channeling and significantly affect fate and transport were not considered in the model (Travis & Rosenberg, 1997). Past work has also shown that sorption heterogeneity, and correlation between heterogeneous sorption and hydraulic conductivity, can have important impacts on contaminant fate and transport (Allen-King et al., 1998). Models that couple these processes with co-metabolism do not presently exist, however.

In addition to the research needs discussed above that deal with modeling specific phenomena or interactions, there is also the need to develop a capability to determine which process is important under given circumstances (site conditions and remedial objectives), and hence, which process should be scrutinized in the most detail during system modeling and design. For instance, if a co-metabolic bioremediation system is to be used as a barrier to contaminant transport, sorption kinetics may not be a very important consideration (Figure 7). In contrast, if the system is to be used to remediate a volume of contaminated groundwater, and a designer is concerned about time to reduce contaminant concentrations to a specified level, then sorption kinetics may be extremely important. Equipped with such information, a remediation practitioner can decide whether gathering data on sorption kinetics is worth the time and money, based upon site-specific conditions and remediation objectives. Similarly, if biodegradation kinetics are shown to occur relatively rapidly when compared with the time-scale of the treatment process, there is likely little need for accurate determination of biodegradation kinetic parameters and a steady-state approximation of biodegradation performance may be adequate.

Summary

Establishing the feasibility of aerobic co-metabolism of chlorinated solvents in the field is a complex task.

The various physical, chemical, and biological processes involved occur over a wide range of scales. Reaction kinetics are the primary concern at the microscale. At the mesoscale, sorption (especially the influence on bioavailability), microbial filtration, and interphase transport are of primary interest. At the macroscale, flow- related processes of advection and dispersion, along with the effects of field heterogeneities, can influence the rate and extent of *in situ* bioremediation. Modeling facilitates the integration of the complexity of the interactions, the variety of phenomena involved, and the range of scales being considered. The modeling examples from the Edwards AFB (McCarty et al., 1998) and Savannah River (Travis & Rosenberg, 1997) sites illustrate that modeling is most effective for gaining understanding of relevant processes, designing bioremediation systems, and predicting system performance. Important knowledge gaps that merit further research include quantitative relationships between microbial growth and permeability reduction, interactions between sorption and biodegradation, the coupling of solute and microbial transport, impact of heterogeneity on co-metabolism, and criteria for selecting pertinent transfer and transformation processes.

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References

Alexander M (1995) How toxic are toxic chemicals in soil? Environ. Sci. Technol. 29: 2713

Allen-King RM, Halket RM, Gaylord DR & Robin MJL (1998) Characterizing the heterogeneity and correlation of perchloroethene sorption and hydraulic conductivity using a facies-base approach. Water Resources Research 34(3): 385–396

Alvarez-Cohen L & Speitel G (2000) Kinetics of aerobic co-metabolism of chlorinated solvents. Biodegradation 12: 105–126 (this issue)

Arp D, Yeager CM & Hyman MR (2000) Molecular and cellular fundamentals of aerobic co-metabolism. Biodegradation 12: 81–103 (this issue)

Ball WP, Curtis GP & Roberts PV (1997a) Physical/chemical processes affecting the subsurface fate and transport of synthetic organic materials. In CH Ward, JA Cherry & MR Scalf (Eds) Subsurface restoration. Ann Arbor Press, Inc., Chelsea, MI, pp. 27–58

Ball WP, Liu C, Xia G & Young DF (1997b) A diffusion-based interpretation of tetrachloroethene concentration profiles in a groundwater aquitard. Water Resources Research 33(12): 2741–2757

Bedient PB, Rifai HS & Newell CJ (1994) Ground water contamination transport and remediation. PTR Prentice Hall, Englewood Cliffs, NJ

Bosma TNP, Middeldorp PJM, Schraa G & Zehnder AJB (1997) Mass transfer limitations of biotransformation: Quantifying bioavailability. Environ. Sci. Technol. 31: 248–252

de Blanc PC, McKinney DC & Speitel Jr GE (1996) A three-dimensional, multi-component model of non-aqueous phase liquid flow and biodegradation in porous media. Proceedings of the ASCE Conference on Non-Aqueous Phase Liquids in the Subsurface Environment. November 10–14, Washington D.C.

Gross MJ, Albinger O, Jewett DG, Logan BE, Bales RC & Arnold RG (1995) Measurement of bacterial collision efficiencies in porous media. Water Res. 29: 1151–1158

Harvey RW & Garabedian SP (1991) Use of colloid filtration theory in modeling movement of bacteria through a contaminated aquifer. Environ. Sci. Technol. 25: 178–185

Herrling B, Stamm J & Buermann W (1991) Hydraulic circulation system for *in situ* bioreclamation and/or *in situ* remediation of strippable contamination. In RE Hinchee & RF Olfenbuttel (Eds) *In situ* Bioreclamation. Butterworth-Heinemann, Stoneham, MA, pp. 173–195

Hopkins GD & McCarty PL (1995) Field evaluation of *in situ* aerobic co-metabolism of trichloroethylene and three dichloroethylene isomers using phenol and toluene as primary substrates. Environmental Science and Technology 29(6): 1628–1637

Jenal-Wanner U & McCarty PL (1997) Development and evaluation of semi-continuous slurry microcosms to simulate *in situ* biodegradation of trichloroethylene in contaminated aquifers. Environmental Science & Technology 31(10): 2915–2922

Kindred JS & Celia MA (1989) Contaminant transport and Biodegradation 2. Conceptual model and test simulations. Water Resources Research 25(6): 1149– 1159

Lang, MM (1995) Design and optimization of *in situ* bioremediation systems relying on co-metabolic degradation. Ph.D. dissertation. Stanford University, Stanford, CA

Lang MM, Roberts PV & Semprini L (1997) Model simulations in support of field scale design and operation of bioremediation based on cometabolic degradation. Ground Water 35(4): 565–573

Martin MJ, Logan BE, Johnson WJ, Jewett DG & Arnold RG (1996) Scaling bacterial filtration rates in different sized porous media. J. Environ. Engng., ASCE. 122: 407–415

McCarty PL & Semprini L (1993) Engineering and hydrogeological problems associated with *in situ* treatment. Hydrological Sciences 38(4): 261–272

McCarty PL, Semprini L, Dolan ME, Harmon TC, Tiedeman C & Gorelick SM (1991) *In situ* methanotrophic bioremediation for contaminated groundwater at St. Joseph, Michigan. In RE Hinchee & RF Olfenbuttel (Eds) On-site bioreclamation. Butterworth-Heinemann, Stoneham, MA, pp. 16–40

McCarty PL, Goltz MN, Hopkins GD, Dolan ME, Allan JP, Kawakami BT & Carrothers TJ (1998) Full-scale evaluation of *in situ* co-metabolic degradation of trichloroethylene in groundwater through toluene injection. Environmental Science and Technology 32(1): 88–100

Mihelcic JR, Lueking DR, Mitzell R & Stapleton, JM (1993) Bioavailability of sorbed- and separate-phase chemicals. Biodegradation 43(3): 141

Nkedi-Kizza P, Biggar, JW, Selim, HM, van Genuchten MTh, Wierenga PJ, Davidson JM & Nielsen DR (1984) On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. Water Resources Research 20(8): 1123–1130

Oya S, Valocchi AJ & Furuichi T (1997) Numerical Modeling of transport and cometabolic degradation of trichloroethylene in groundwater, Journal of Groundwater Hydrology (Japan) 39(1): 17–31

Rajagopolan R & Tien C (1976) Trajectory analysis of deep-bed filtration with the sphere-in-cell porous media model. AIChE J. 22: 523–533

Rijnaarts HHM, Norde W, Bouwer EJ, Lyklema J & Zehnder AJB (1996) Bacterial deposition in porous media related to the clean bed collision efficiency and to substratum blocking by attached cells. Environ. Sci. Technol. 30(10): 2869–2876

Semprini L, McCarty PL, Dolan ME, Lang MM, McDonald T, Bae J & Kitanidis P (1992) Design and treatability study of *in situ* bioremediation of chlorinated aliphatics by methanotrophs at St. Joseph, Michigan. In Bioremediation of hazardous wastes. EPA Office of Research and Development Report EPA/600/R-92/126, pp. 43–45

Semprini L & McCarty PL (1991) Comparison between model simulations and field results for *in situ* biorestoration of chlorinated aliphatics: Part 1. Biostimulation of methanotrophic bacteria. Ground Water 29(3): 365–374

Semprini L & McCarty PL (1992) Comparison between model simulations and field results for *in situ* biorestoration of chlorinated aliphatics: Part 2. Co-metabolic transformations. Ground Water 30(1): 37–44

Sturman PJ, Stewart PS, Cunningham AB, Bouwer EJ & Wolfram JH (1995) Engineering scale-up of *in situ* bioremediation processes: A review. Journal of Contaminant Hydrology 19: 171–203

Tompson AFB, Knapp RB, Hanna ML & Taylor RT (1994) Simulation of TCE migration and biodegradation in a porous medium under conditions of finite degradation capacity. Advances in Water Resources 17: 241–249

Travis BJ & Rosenberg ND (1997) Modeling *in situ* bioremediation of TCE at Savannah River: Effects of product toxicity and microbial interactions on TCE degradation. Environ. Sci. Technol. 31: 3093–3102

Voice TC, Zhao X & Maraqa MA (1997) Desorption/biodegradation interactions in laboratory soil columns. American Chemical Society Division of Environmental Chemistry Preprints of Extended Abstracts 37(2): 245–246

Yao K-M, Habibian MT & O'Melia CR (1971) Water and waste water filtration: Concepts and applications. Environ. Sci. Technol. 5: 1105–1112

Zhang W, Bouwer EJ & Ball WP (1998) Bioavailability of hydrophobic organic contaminants: Effects and implications of sorption-related mass transfer on bioremediation. Ground Water Monitoring and Remediation 18(1): 126–138