A numerical model (MISER) for the simulation of coupled physical, chemical and biological processes in soil vapor extraction and bioventing systems

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Abstract

The efficiency and effectiveness of soil vapor extraction (SVE) and bioventing (BV) systems for remediation of unsaturated zone soils is controlled by a complex combination of physical, chemical and biological factors. The Michigan soil vapor extraction remediation (MISER) model, a two-dimensional numerical simulator, is developed to advance our ability to investigate the performance of field scale SVE and BV systems by integrating processes of multiphase flow, multicomponent compositional transport with nonequilibrium interphase mass transfer, and aerobic biodegradation. Subsequent to the model presentation, example simulations of single well SVE and BV systems are used to illustrate the interplay between physical, chemical and biological processes and their potential influence on remediation efficiency and the pathways of contaminant removal. Simulations of SVE reveal that removal efficiency is controlled primarily by the ability to engineer gas flow through regions of organic liquid contaminated soil and by interphase mass transfer limitations. Biodegradation is found to play a minor role in mass removal for the examined SVE scenarios. Simulations of BV systems suggest that the effective supply of oxygen may not be the sole criterion for efficient BV performance. The efficiency and contaminant removal pathways in these systems can be significantly influenced by interdependent dynamics involving biological growth factors, interphase mass transfer rates, and air injection rates. Simulation results emphasize the need for the continued refinement and validation of predictive interphase mass transfer models applicable under a variety of conditions and for the continued...
elucidation and quantification of microbial processes under unsaturated field conditions. Published by Elsevier Science B.V.

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1. Introduction

Soil vapor extraction (SVE) and bioventing (BV) are related in situ remediation techniques for unsaturated soils contaminated with organic compounds, particularly petroleum hydrocarbons. SVE and BV are similar, in that they both employ vadose zone wells and pumps to generate gas flow through the unsaturated zone, but differ fundamentally in the mechanism of contaminant removal. SVE systems emphasize removal by contaminant volatilization and above ground recovery (Johnson et al., 1994). Alternatively, BV systems are designed to minimize contaminant recovery, removing contaminants by in situ biodegradation which is stimulated by the enhanced supply of oxygen from the air stream (Dupont, 1993; Hinchee, 1994). Both SVE and BV are popular and widely used, owing to their proven effectiveness, capacity for flexible design and operation, comparatively simple and nonintrusive implementation, and cost competitiveness (Pedersen and Curtis, 1991; Rathfelder et al., 1995).

Despite the effectiveness and flexibility of SVE/BV technologies, their efficiency and degree of success is controlled by a complex combination of physical, chemical and biological factors. SVE systems characteristically exhibit large initial contaminant exhaust concentrations followed by rapid drop off and extended periods of low-level removal. Diminishing removal efficiency and long term tailing behavior can partly reflect the preferential removal of more volatile constituents (Hoag et al., 1984), but are more often considered indicative of diffusion controlled contaminant transport from regions with diminished access to the flow stream (Johnson et al., 1994). Contaminant occlusion may result from local variations in porosity or fluid distribution (Brusseau, 1991; Gierke et al., 1992; Cho et al., 1993), flow bypassing in heterogeneous soils (Kearl et al., 1991; Ho and Udell, 1992; Imhoff and Jaffe, 1994), or may result from operational factors such a vacuum induced water table upwelling (Johnson et al., 1990). Other evidence indicates that removal efficiency can be constrained by rate-limited interphase mass transfer in the volatilization of non-aqueous phase liquids (NAPL) (Hayden et al., 1994; Wilkins et al., 1995), air–water interphase exchange (Armstrong et al., 1994; Fisher et al., 1996), or in rate-limited desorption (Brusseau, 1991; Grathwohl and Reinhard, 1993; Croise et al., 1994; Wehrle and Brauns, 1994; Abriola et al., 1999).

Complex interdependent processes similarly affect the efficiency and performance of BV systems. Laboratory studies suggest that under partially saturated conditions, higher rates of biotransformation occur at higher levels of soil moisture (Fan and Scow, 1993; Lee and Swindoll, 1993) and that this dependence may be compound specific (Holman and Tsang, 1995). In accordance with these studies, the addition of soil moisture at some BV field sites has been reported to enhance degradation rates (Zwick et al., 1997). At other sites, however, the addition of soil moisture had little effect (Miller, 1990) or was found to diminish BV performance due to the restriction of oxygen delivery (Miller et
Degradation rates have also been linked to the addition of inorganic nutrients in laboratory experiments (Dupont, 1993; Baker et al., 1994) and in field applications (Bulman et al., 1993; Breedveld et al., 1995; Gruiz and Kriston, 1995; Möller et al., 1996). Other analysis, however, has suggested a weak correlation between nutrient addition and enhanced oxygen utilization (Leeson et al., 1995). Moreover, the influence of nutrient addition may be difficult to distinguish from that of soil moisture addition which is frequently the method used to deliver nutrients (Dupont et al., 1991). Degradation rates also depend on substrate availability which can be limited by the rate of desorption (Scow, 1993; Fry and Istok, 1994). Inhibition of biodegradation at high concentrations of inorganic nutrients (Baker et al., 1994) or high concentrations of organic substrates (Speitel and Alley, 1991; Huesemann and Moore, 1994; Mu and Scow, 1994) has been observed in laboratory studies. The significance of inhibition in field operations, however, has received limited attention. Variations in design parameters may also create tradeoffs between supply of oxygen (flow rate) and contaminant dispersal and mobilization beyond the initial contamination region. Contaminant redistribution can result in losses to the atmosphere (Lang et al., 1997) or contaminant mobilization into subsurface structures, where health and safety hazards are of concern.

The studies cited above represent advances in the recognition and characterization of specific processes influencing SVE/BV systems. They also highlight the difficulties inherent in understanding the combined and interdependent influence of physical, chemical and biological processes on system performance. The efficiency of specific SVE/BV systems is therefore difficult to predict. Consequently the design, operation, and assessment of these systems is often based on experience and broad design criteria (e.g. Johnson et al., 1990; DePaoli, 1996). Numerical simulation models can provide a means to integrate processes isolated at laboratory scales with the complexity of field settings, and have therefore been advanced as research tools for studying and elucidating dynamics in SVE/BV systems. Existing simulation models applicable to SVE/BV systems vary in their focus and processes considered. Simulation models considering only gas flow behavior have been used for analysis of pneumatic pump tests (Baehr and Hult, 1991; Massmann and Madden, 1994) and for the assessment and design of SVE (Sepehr and Samani, 1993) and BV systems (Mohr and Merz, 1995). A more complex group of models couples analytical or numerical transport solutions with single-phase gas flow solutions (Baehr et al., 1989; Rathfelder et al., 1991; Benson et al., 1993; Zaidel and Russo, 1993). Further levels of sophistication are found in models that include one or more enhancements for multiphase flow processes (Sleep and Sykes, 1989), the simulation of nonequilibrium interphase exchange (Gierke et al., 1990; Brusseau, 1991; Armstrong et al., 1994; Poulsen et al., 1996), and the inclusion of biodegradation processes (McClure and Sleep, 1996). Among these, the most sophisticated are those of McClure and Sleep (1996) and Poulsen et al. (1996). Each, however, exhibits limitations in its general applicability to field problems by focusing only on single phase fluid flow conditions, by neglecting biotransformation, or by failing to fully account for nonequilibrium mass transfer processes.

This paper presents a field scale SVE/BV simulator specifically designed to integrate major processes identified in the foregoing literature review, including: multiphase flow, multicomponent compositional transport with nonequilibrium interphase mass transfer,
and Monod kinetics for aerobic biodegradation. The two-dimensional model is referred to as the Michigan soil vapor extraction remediation model (MISER). Following model presentation, representative values for interphase mass transfer and aerobic biodegradation are obtained from a literature review and are employed in illustrative simulations to explore the influence of system design, nonequilibrium mass exchange, and biological growth factors on SVE/BV system efficiency and performance.

2. Conceptual and mathematical formulation fluid phases

2.1. Fluid phases

Model formulation is based upon a conceptualization of the soil/fluid system as depicted in Fig. 1. Three fluid phases are modeled in MISER: an immobile residual
organic liquid, a mobile gas phase, and a mobile aqueous phase. The gas and aqueous phases can flow simultaneously in response to pressure and density gradients arising from fluid extraction or injection at wells, natural recharge, and applied surface irrigation. The movement of these phases is described by standard macroscopically averaged flow equations (Abriola, 1989),

\[
\frac{\partial}{\partial t} \left( \phi \rho^*_\alpha S^*_\alpha \right) - \nabla \cdot \left[ \rho^*_\alpha \lambda^*_\alpha \left( \nabla P^*_\alpha - \rho^*_\alpha g \right) \right] = E^*_\alpha + \rho^*_\alpha Q^*_\alpha \quad \alpha = a, g
\]

where \( \alpha \) denotes the phases (\( g = \) gas, \( a = \) aqueous); \( \phi \) is the porosity of the assumed incompressible soil matrix; \( \rho^*_\alpha \) is the fluid phase mass density; \( S^*_\alpha \) is the fluid phase saturation; \( \lambda^*_\alpha = kk^*_\alpha / \mu^*_\alpha \) is the phase mobility; \( k \) is the intrinsic permeability tensor; \( \mu^*_\alpha \) is the fluid phase dynamic viscosity; \( P^*_\alpha \) is fluid pressure; \( g \) is the gravitational acceleration vector; \( E^*_\alpha = \Sigma_\beta \Sigma_\beta E^*_{\alpha\beta} \), where \( E^*_{\alpha\beta} \) is the rate of interphase mass transfer to phase \( \alpha \) from all contiguous phases \( \beta \) (accumulated for components, \( c \)) per volume of porous medium; and \( Q^*_\alpha \) is the source/sinks of phase \( \alpha \).

Due to the conceptual difficulty in tracking the pressure of NAPL at an immobile residual saturation, MISER assumes that the aqueous phase saturation is independent of the NAPL residual and is related solely to two phase gas–aqueous retention data. The van Genuchten type function (van Genuchten, 1980) is used to represent retention data, and relative permeability expressions for the mobile aqueous and gas phases are evaluated with the model of Parker et al. (1987). Hyteresis in the retention and relative permeability functions is neglected. Changes in the assumed immobile NAPL saturation occur solely by interphase mass transfer since no internal sources/sinks of organic liquid are considered. NAPL (\( \alpha \)) saturation is updated from a NAPL mass balance equation,

\[
\frac{\partial}{\partial t} \left( \phi \rho^*_\alpha S^*_\alpha \right) = E^*_\alpha
\]

2.2. Phase composition

A compositional modeling approach is employed in MISER, with each of the phases comprised by a variable number of components (see Fig. 1). The transport and transformation of individual phase components of the mobile aqueous and gas phases are described by a general macroscopically averaged transport equation (Abriola, 1989),

\[
\frac{\partial}{\partial t} \left( \phi S^*_\alpha \rho^*_\alpha x^*_\alpha \right) + \nabla \cdot \phi S^*_\alpha \left( \rho^*_\alpha x^*_\alpha V^*_\alpha - \rho^*_\alpha D^*_\alpha \nabla x^*_\alpha \right) = E^*_\alpha B^*_\alpha \quad \alpha = a, g
\]

where the subscript \( c \) denotes components of phase \( \alpha \); \( \rho^*_\alpha \) is the phase molar density; \( x^*_\alpha \) is the component mole fraction in phase \( \alpha \); \( V^*_\alpha \) the phase velocity; \( D^*_\alpha \) is the phase hydrodynamic dispersion tensor for component \( c \); \( E^*_\alpha B^*_\alpha \) is the net interphase mole
transfer rate of component \( c \) to phase \( \alpha \) from contiguous phases \( \beta \); and \( B_{\alpha\beta} \) is the net rate of moles of component \( c \) consumed by biological transformation and is restricted to the aqueous phase. The phase velocity in Eq. (3) is related to the phase pressure and density gradient by a standard extension of Darcy’s Law (Abriola, 1989).

\[
\phi S_a V_a = -\lambda_a \left( \nabla P_a - \rho_a^* g \right) \quad \alpha = a, g
\]

The hydrodynamic dispersion tensor is evaluated with a traditional groundwater modeling approach (Bear, 1972), wherein the tortuosity factor is computed as a function of fluid content (Millington and Quirk, 1961).

Constituents in the immobile organic (o) and solid (s) phases are not subject to transport by advection and it is further assumed that macroscopic diffusive transport within these phases is negligible. The transport equations for these phases are, then, expressed as:

\[
\frac{\partial}{\partial t} \left( \phi S_a \rho_o x_o \right) = E_{oa} + E_{go},
\]

\[
\rho_s \frac{\partial}{\partial t} \left( \omega_s \right) = E_{sa},
\]

where \( \omega_s \) is the sorbed mass of component \( c \) per mass of soil and \( \rho_s^* \) is the bulk solid phase density. Here, variations in \( \rho_s^* \) with time have been neglected.

### 2.3. Interphase mass transfer

Rate limited interphase mass transfer is modeled with a linear driving force expression (Weber and DiGiano, 1996)

\[
E_{\alpha\beta} = \rho_\alpha K_{\alpha\beta} (x_\alpha^e - x_\alpha),
\]

where \( \alpha \) is the controlling phase, \( K_{\alpha\beta} \) is the effective mass transfer rate coefficient between the \( \alpha-\beta \) phases, and \( x_\alpha^e \) is the \( \alpha \) phase mole fraction of component \( c \) in equilibrium with the mole fraction of \( c \) in phase \( \beta \). This expression is used to model the volatilization and dissolution of the NAPL, sorption of the NAPL components from the aqueous phase, and gas–aqueous interphase exchange of all components. Mass transfer resistance across all interfaces is assumed to occur within the aqueous phase, with the exception of the NAPL–gas interface, where it is assumed to occur within the gas phase.

Equilibrium mole fractions for partitioning between the fluid phases are evaluated from equilibrium partitioning relations based on appropriate forms of Raoult’s Law and Henry’s Law under the assumption of ideal fluid behavior (Adenekan et al., 1993; Schwarzenbach et al., 1993). The equilibrium sorption capacity is represented by a nonlinear Freundlich isotherm,

\[
\omega_{si} = K_f C_{ai}^{1/n_i},
\]

where \( K_f \) and \( n_i \) are the Freundlich coefficients for component \( c \), and \( C_{ai} \) is the aqueous phase concentration of component \( c \).
2.4. Biotransformations

Biodegradation is modeled solely as an aerobic process and is assumed to occur only within the aqueous phase by an indigenous, spatially heterogeneous, mixed microbial population that is present as attached microcolonies. It is further assumed that biomass growth does not affect soil permeability, there is no biomass transport and detachment or sloughing of the attached biofilm is negligible. Monod-type kinetic expressions are employed to describe biophase utilization of substrates, electron acceptor, and a single limiting nutrient (Williamson and McCarty, 1976; Bailey and Ollis, 1986; Chen et al., 1992),

\[
B_{bl} = -F_{i}k_{i}X\left(\frac{x_{bl}}{K_{s_{i}} + x_{bl}}\right)\left(\frac{x_{SO_{2}}}{K_{s_{i}O_{2}} + x_{SO_{2}}}\right)\left(\frac{x_{bN}}{K_{s_{i}N} + x_{bN}}\right)I_{i}I_{O_{2}}
\]

where subscripts \(l\), \(b\), \(O\), and \(N\) denote the substrate, biophase, oxygen, and nutrient, respectively; \(F_{i}\) is the use coefficient of component \(c\) with substrate \(l\) degradation \((F_{i} = 1 \text{ for } c = l)\); \(k_{i}\) is the maximum specific substrate utilization rate; \(X\) is the active biomass concentration; \(K_{s_{i}}\) is the half-saturation coefficient of component \(c\); and \(I_{i}\) and \(I_{O_{2}}\) are substrate and oxygen inhibition functions described below. When \(c\) is \(O_{2}\) or \(N\), Eq. (9) is summed over all the degradable organic components. MISER has the capability to simulate biophase uptake of substrate and oxygen as either instantaneous or rate-limited. Due to the lack of mass transfer information, however, all simulations presented herein assume biophase uptake from the aqueous phase occurs as an instantaneous process.

MISER incorporates inhibitory effects on biokinetics resulting from the presence of excessively high or low substrate concentrations, or due to the presence of oxygen below a minimum threshold limit. Inhibitory effects from substrate concentrations are modeled with the expressions (Wood et al. 1994),

\[
I_{i} = \left(1 - \frac{x_{\text{min}}}{x_{a_{i}}}\right)\left(1 - \frac{x_{a_{i}}}{x_{\text{max}}^{a_{i}}}\right)
\]

where \(x_{\text{min}}\) is the minimum detectable limit of substrate \(l\), and \(x_{\text{max}}^{a_{i}}\) is the inhibitory mole fraction of substrate \(l\). Laboratory studies have found that aerobic degradation of aromatic hydrocarbons is greatly diminished or ceases entirely under hypoxic conditions (oxygen concentrations below 2 ppm) and in the absence of nitrate as an alternative electron acceptor (Chiang et al., 1989; Leahy and Olsen, 1997). An empirical inhibition function is used to represent effects of reduced degradation rates under hypoxic conditions,

\[
I_{O_{2}} = \left(1 - \frac{x_{\text{min}}^{SO_{2}}}{x_{SO_{2}}}\right)
\]

where \(x_{\text{min}}^{SO_{2}}\) is the threshold oxygen mole fraction below which aerobic metabolism ceases.
Growth and decay of the attached microbial population is modeled with a Monod-type kinetic expression (Chen, 1996),

\[
\frac{dX}{dt} = \sum Y_i \left( \frac{x_{bl}}{K_{x_{bl}} + x_{bl}} \right) \left( \frac{x_{bN}}{K_{x_{bN}} + x_{bN}} \right) \left( I_{o_2} I_{\text{max}} - K_d I_{\text{min}} \right) X
\]

where \(Y_i\) is the yield coefficient for metabolism of substrate \(i\); \(I_{\text{min}} = 1 - (X_{\text{min}}/X)\) and \(I_{\text{max}} = 1 - (X/X_{\text{max}})\) are functions constraining the biomass concentration between a minimum value, \(X_{\text{min}}\), reflecting the indigenous population present in uncontaminated subsurface environments and a maximum permitted biomass concentration, \(X_{\text{max}}\), due to predation or mass transfer limitations (Zysset et al., 1994); and \(K_d\) is the decay coefficient of the microorganisms.

3. Numerical solution approach

MISER solves the governing flow (Eq. 1) and transport (Eq. 3) equations in two space dimensions; either within a cross-sectional \(x-z\) domain, or an axisymmetric \(r-z\) domain. Numerical solutions are obtained with a standard Galerkin finite element approach using linear triangular elements (Huyakorn and Pinder, 1983). A set-iterative solution algorithm is employed to reduce the size of solution matrices and enhance flexibility (Reeves and Abriola, 1994). In this approach, the flow, transport and biodegradation equations are decoupled and solved separately. Decoupling the equation sets is achieved by lagging the coupling terms within the iteration scheme (phase density, molecular weight, interphase exchange, and bioreaction), either by a time step or an iteration. The mobile phase flow equations (Eq. 1) are solved first using a pressure based simultaneous solution scheme and Quasi-Newton iteration to account for nonlinearities (Huyakorn and Pinder, 1983). The mobile phase velocities are then updated with a finite element solution of Eq. 4. Subsequently, the entire set of constituent transport equations (Eq. 3) for the mobile and immobile phases is solved sequentially, employing a Picard iteration method. Phase density and phase molecular weight are updated within the iteration loop. NAPL saturations (Eq. 2), mass exchange terms (Eq. 7), and bioreactions (Eqs. 9 and 12) are time lagged and updated at the start or end of each time step. Time steps vary in response to flow and transport conditions and are self-adaptively adjusted based on the convergence rate. Time steps are typically constrained to less than 1 h. A more detailed description of the numerical procedures can be found in Abriola et al. (1997). The model has been verified mathematically through global mass balance computations, comparisons with one- and two-dimensional analytical solutions, and intermodel simulation comparisons (Abriola et al., 1997).

4. Parameter estimation

The numerical simulation of SVE/BV systems requires a large number of parameters to describe the coupled physical, chemical and biological processes. Many of these
parameters are not routinely or easily measured in field and/or laboratory settings and may therefore be difficult to estimate. This is particularly true of interphase mass transfer and microbial transformation rates. Since the validity of numerical solutions depends strongly on the reasonable evaluation of such parameters, a literature review was undertaken to establish a range of values for mass transfer and biodegradation parameters.

4.1. NAPL–gas and NAPL–aqueous effective mass transfer coefficients

Rate limited NAPL volatilization has been observed in several laboratory SVE experiments. Explanations of mass transfer limitations reflect, to a large degree, the experimental conditions, and suggest that several physical processes may contribute to observed disequilibrium gas phase concentrations in the presence of NAPL. Explanations of mass transfer limitations include: diffusional flux across the boundary layer which diminishes in proportion to the equilibrium flux with increasing gas discharge (Kearl et al., 1991; Lange and Mull, 1994; Wilkins et al., 1995); preferential flow paths resulting from nonuniform fluid distribution (Rainwater et al., 1989; Abriola et al., 1999); flow bypassing due to heterogeneous permeability distribution (Kearl et al., 1991; Ho and Udell, 1992); and diminishing mole fractions in the organic liquid (Hayden et al., 1994).

Although a number of laboratory experiments have demonstrated the occurrence of rate limited NAPL volatilization in SVE/BV systems, quantification of NAPL–gas mass transfer rates has been reported in only a few studies (Wilkins et al., 1995; Abriola et al., 1999), and no comparable work was found on the estimation of NAPL–gas effective mass transfer coefficients from field scale measurements. In Wilkins et al. (1995), the NAPL–gas effective mass transfer coefficients were estimated from venting experiments in laboratory columns containing a variety of well-characterized soils. Measured effluent gas concentrations were found to deviate from equilibrium with the magnitude of disequilibrium increasing with gas flow. A multivariate regression analysis yielded a strong correlation of $K_{pg}$ as a function of soil, chemical and flow properties.

Due to the scarcity of available NAPL–gas mass transfer data, numerical models which include processes of nonequilibrium NAPL–gas mass transfer have typically used estimated ranges of effective mass transfer coefficients. Literature reported values of NAPL–gas effective mass transfer coefficients from experimental and numerical investigations are listed in Table 1, indicating a considerable range in magnitude. This table suggests NAPL–gas effective mass transfer coefficients could range from approximately $10$–$1000$ day$^{-1}$ over gas discharges from $1$–$20$ m day$^{-1}$.

A large body of literature exists on NAPL dissolution rates in saturated systems (e.g. Powers et al., 1990). Rates of NAPL dissolution have been correlated with aqueous velocity, and rate limitations have generally been observed at high aqueous velocities. In unsaturated systems, aqueous velocities are typically small, and thus concentrations in adjacent aqueous–NAPL phases are likely to be in equilibrium. In this work, simulations use a relatively large aqueous–NAPL effective mass transfer coefficient, which produces near equilibrium conditions in numerical simulations (Sleep and Sykes, 1989).
Table 1
Measured and estimated values of NAPL–gas effective mass transfer coefficients in SVE systems

<table>
<thead>
<tr>
<th>$K_{eq}$ (1 day$^{-1}$)</th>
<th>$q$ (m day$^{-1}$)</th>
<th>Reference</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1–0.5</td>
<td>0–0.3</td>
<td>Sleep and Sykes (1989)</td>
<td>Estimated values used in numerical simulation of field scale SVE</td>
</tr>
<tr>
<td>2.5–19,300</td>
<td>4–63</td>
<td>Rathfelder et al. (1991)</td>
<td>Values obtained from laboratory data with porous beads; used in exploratory one-dimensional simulations</td>
</tr>
<tr>
<td>1000–6500</td>
<td>25–430</td>
<td>Wilkins et al. (1995)</td>
<td>Obtained by fitting to effluent data from controlled column venting experiments</td>
</tr>
<tr>
<td>5300</td>
<td>24.4</td>
<td>Abriola et al. (1999)</td>
<td>Fit to column venting data</td>
</tr>
<tr>
<td>0.1–100</td>
<td>–</td>
<td>Poulsen et al. (1996)</td>
<td>Values estimated based on literature review; used in simulations of field scale SVE</td>
</tr>
</tbody>
</table>

4.2. Aqueous–gas effective mass transfer coefficients

Considerably, more information is available on interphase solute exchange between the aqueous and vapor phases. Previous relevant work is found in the literature on trickle bed systems, which showed that the rates of interphase mass transfer depend on flow rate and chemical and medium properties. Laboratory studies pertinent to subsurface systems (i.e. lower flow rates) demonstrate varying degrees of nonequilibrium exchange rates between aqueous and vapor phases (Cho and Jaffe, 1990; Cho et al., 1993; Gierke et al. 1990, 1992; Berndtson and Bunge, 1991; Imhoff and Jaffe, 1994; Szatkowski et al., 1995). Correlations for the aqueous–gas effective mass transfer coefficient as a function of flow conditions and fluid and medium properties were developed by Cho et al. (1993) and Szatkowski et al. (1995). Table 2 summarizes reported values of

Table 2
Representative values of aqueous–gas effective mass transfer coefficients

$Sh'$ = modified Sherwood number = $K_{eq}d_0^2/D_a$; 1(3) = 1 × 10$^3$.

<table>
<thead>
<tr>
<th>$K$ (1 day$^{-1}$)</th>
<th>$Sh'$</th>
<th>Reference</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td>9.1(–2)</td>
<td>Gierke et al. (1990)</td>
<td>Estimated from correlations for trickle bed reactors</td>
</tr>
<tr>
<td>7.9(–3)–0.24</td>
<td>5(–5)–1.5(–3)</td>
<td>Cho et al. (1993)</td>
<td>Fit to data from column infiltration experiments</td>
</tr>
<tr>
<td>1.73, 3.46</td>
<td>2(–3), 4(–3)</td>
<td>Armstrong et al. (1994)</td>
<td>Fit to data from emplaced box SVE field experiments</td>
</tr>
<tr>
<td>24, 168</td>
<td>0.14–0.97</td>
<td>Imhoff and Jaffe (1994)</td>
<td>Fit to data from countercurrent column experiments</td>
</tr>
<tr>
<td>17–86</td>
<td>0.3–1.5</td>
<td>Szatkowski et al. (1995)</td>
<td>Fit to data from laboratory experiments using toluene</td>
</tr>
<tr>
<td>0.17–0.86</td>
<td>2.3(–3)–1.1(–2)</td>
<td>Fisher et al. (1996)</td>
<td>Fit to laboratory sandbox venting data</td>
</tr>
</tbody>
</table>
aqueous–gas effective mass transfer coefficients. It should be cautioned that values are not directly comparable due to differences in the experimental conditions.

Studies directly relevant to SVE/BV systems have been reported in which effluent concentration data from SVE experiments were used to fit aqueous–gas effective mass transfer coefficients (Armstrong et al., 1994; Fisher et al., 1996). In Armstrong et al. (1994), data from an emplaced box SVE field experiment were used to fit two models incorporating first order nonequilibrium kinetics for air–water and aqueous–solid exchange. These investigators conclude that air–water mass transfer was the dominant process controlling removal efficiency and that the kinetic coefficients are site dependent and best obtained by calibration. Fisher et al. (1996) conducted SVE experiments in a laboratory sandbox, focusing on the influence of variable moisture content and multicomponent organics. Observed rate-limiting behavior was attributed solely to the aqueous–gas mass exchange due to use of nonsorbing quartz sand. Kinetic coefficients determined by model calibration were found to depend on moisture content, and in some data sets, time varying effective mass transfer coefficients were required to match the experimental data.

Explanations of observed nonequilibrium mass transfer behavior generally involve the sequestering of contaminants in regions with diminished access to the flow stream. Several researchers suggest that mass transfer resistance at the aqueous–gas interface is negligible (Brusseau, 1991; Gierke et al., 1992) and/or that observed disequilibrium is the result of diffusional resistance from immobile water within soil aggregates (Cho and Jaffe, 1990; Cho et al., 1993; Brusseau, 1991; Gierke et al., 1992; Imhoff and Jaffe, 1994) or immobile interparticle water (Fisher et al., 1996). Others note that the flow regime may additionally be a critical factor affecting the observed mass transfer behavior (Imhoff and Jaffe, 1994; Szatkowski et al., 1995). Preferential flow can effectively increase the diffusion length to the flow stream, reducing overall effective mass transfer coefficients. Imhoff and Jaffe (1994) used tracer tests to show that flow conditions in their system were more uniform than in earlier experiments conducted by Cho et al. (1993), providing a likely explanation for mass transfer rates 10–40 larger than those measured by Cho et al. (1993).

The studies above suggest that aqueous–gas effective mass transfer coefficients in SVE/BV systems should generally range on the order of 0.1–10.0 day$^{-1}$ and that values are likely to be dynamic in space and time depending on flow and moisture conditions.

4.3. Aqueous–solid effective mass transfer coefficients

Because sorption processes may substantially influence solute transport behavior, considerable attention has been directed to the measurement and elucidation of nonequilibrium sorption mechanisms (e.g. Brusseau et al., 1991; Weber et al., 1991, 1992). Sorption rate data from batch and column experiments have been fit with a number of sorption models, and rate constants have been found to vary over seven orders of magnitude, depending on sorbate and sorbent properties, as well as the fitting model. Table 3 presents a sample of published rate constants.
Table 3
Sample of reported values of aqueous–solid effective mass transfer coefficients

<table>
<thead>
<tr>
<th>$K_m$ (1 day$^{-1}$)</th>
<th>Reference</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1–2.8</td>
<td>Miller and Weber (1986)</td>
<td>Single site first order model fit to sorption data with moderately hydrophobic solutes and sands</td>
</tr>
<tr>
<td>72–120</td>
<td>Lee et al. (1988)</td>
<td>Bicontinuum model fit to sorption data with hydrophobic solutes and low organic sands</td>
</tr>
<tr>
<td>0.3–0.8</td>
<td>Weber and Miller (1988)</td>
<td>Bicontinuum model fit to sorption data for moderately hydrophobic solutes and sands</td>
</tr>
<tr>
<td>0.008–187</td>
<td>Brusseau and Rao (1989)</td>
<td>Compilation of literature data</td>
</tr>
<tr>
<td>72, 240</td>
<td>Brusseau (1991)</td>
<td>Simulation of columns venting experiments; coefficients determined from an empirical correlation</td>
</tr>
<tr>
<td>4.3</td>
<td>Armstrong et al. (1994)</td>
<td>Fit to data from emplaced box SVE field experiments</td>
</tr>
<tr>
<td>3.1</td>
<td>Abriola et al. (1999)</td>
<td>Fit to column venting data</td>
</tr>
<tr>
<td>0.095–690</td>
<td>Croise et al. (1994)</td>
<td>Time varying rate coefficients required for calibration with venting data</td>
</tr>
</tbody>
</table>

Laboratory venting experiments have demonstrated that nonequilibrium desorption kinetics can constrain the efficiency of contaminant recovery in SVE systems (Grathwohl and Reinhard, 1993; Grathwohl et al., 1990; Wehrle and Brauns, 1994), and effluent data from such experiments have been used to quantify desorption rate coefficients. The venting data of Grathwohl et al. (1990) and Wehrle and Brauns (1994) were fit by Croise et al. (1994) with a transport model incorporating first order kinetics for aqueous–gas and aqueous–solid mass transfer. Desorption was found to be the rate limiting step. Calibration, however, was unsuccessful when the rate coefficient was held constant and could only be achieved when the desorption rate coefficient was allowed to diminish with time over three orders of magnitude. Desorption was similarly found to be the rate limiting step in venting experiments conducted by Wilkins et al. (1995). Here also, a fit of a first order desorption model was found to provide reasonable agreement only for early time effluent data (Abriola et al., 1999). An improved fit over early and long time data was obtained with a multiple compartment modeling approach incorporating slow, medium and fast desorption processes (Grathwohl and Reinhard, 1993).

There is little information available on sorption kinetics in field scale SVE/BV systems. First order desorption was employed to model effluent data from an emplaced box SVE field experiment (Armstrong et al., 1994), but the effluent data were insufficient to provide a good fit for $K_m$ and this parameter did not have a substantial impact on predicted effluent concentrations. Inclusion of rate limited desorption, however, was shown to have a significant influence on the predicted mass remaining in the system. Collectively, the laboratory and field data for SVE systems suggest that aqueous–solid effective mass transfer coefficients may range over three orders of magnitude (0.1–10 day$^{-1}$) for sandy aquifer material.

4.4. Biodegradation parameters

Data on rates of oxygen utilization and biodegradation of organic compounds in connection with BV systems are limited in their availability and subjected to uncertainty.
Biodegradation capacity in BV systems is often assessed in terms of oxygen consumption measured by in situ respirometry (Hinchee, 1994). Equivalent zero-order hydrocarbon consumption rates based on conversion of oxygen consumption rates have been reported between 2 and 20 mg/kg day \(^{-1}\) for JP-4 jet fuel (Hoeppel et al., 1991) and 1–33 mg/kg day \(^{-1}\) for diesel fuel (Moller et al., 1996). It is unclear, however, whether

<table>
<thead>
<tr>
<th>Table 4</th>
<th>Ranges of biological parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Parameter</td>
<td>Range</td>
</tr>
<tr>
<td>(k_i) (1 day (^{-1}))</td>
<td>0.01–4</td>
</tr>
<tr>
<td></td>
<td>0.01–9.9</td>
</tr>
<tr>
<td>(K_{so,1}) (mg/l)</td>
<td>0.56–0.87</td>
</tr>
<tr>
<td></td>
<td>0.044–20.0</td>
</tr>
<tr>
<td></td>
<td>0.03–15.9</td>
</tr>
<tr>
<td>(K_{so,2}) (mg/l)</td>
<td>0.01–8.0</td>
</tr>
<tr>
<td>(Y_i) (g/g)</td>
<td>0.4–0.6</td>
</tr>
<tr>
<td></td>
<td>0.01–1.56</td>
</tr>
<tr>
<td>(F_{O_2}) (1 day (^{-1}))</td>
<td>1.85–3.19</td>
</tr>
<tr>
<td>(K_d) (1 day (^{-1}))</td>
<td>0.01–0.2</td>
</tr>
<tr>
<td>(x_{\text{max}}) (expressed mg/l)</td>
<td>290</td>
</tr>
<tr>
<td>(x_{\text{min}}) (expressed mg/l)</td>
<td>1–2</td>
</tr>
<tr>
<td>(X) (cells/g soil)</td>
<td>1(4)–1(6)</td>
</tr>
<tr>
<td></td>
<td>3(5)–1(8)*</td>
</tr>
<tr>
<td></td>
<td>1(3)–7(9)</td>
</tr>
</tbody>
</table>

*Units not specified; assumed as cells/g soil, 1(3) = 1×10^3.
degradation rates determined by oxygen consumption are representative of actual degradation rates during BV (Hoeppel et al., 1991). This issue was investigated by Moller et al. (1996) who compared zero-order hydrocarbon degradation rates determined by oxygen consumption and soil measurements. They found good correlation only during early time periods and postulated that lack of agreement during later periods could have resulted from buildup of degradation products and variation in subsurface temperature. Moreover, the estimation of total remediation time based on zero- and first-order reaction rates were substantially different, with estimates based on first-order rates thought to be more representatives over the entire remediation period.

Other researchers have noted that both zero- and first-order approximations can provide poor representation of biotransformation rates when applied outside the valid range of approximation (Bekins et al., 1998; Chen and Abriola, 1998). Monod kinetics are considered more representative because they span both zero- and first-order reaction rates. However, most studies estimate aerobic biodegradation rates with first-order kinetic parameters, and there are a limited number of studies which have estimated full Monod kinetic parameters (Essaid et al., 1995). Table 4 lists reported ranges of Monod and biodegradation parameters. Many of the values listed in Table 4 are from literature reviews conducted by Essaid et al. (1995) and Chen (1996), and primarily represent Monod parameters for aerobic biodegradation processes in saturated systems. Applying these saturated zone parameter values to unsaturated systems presumes that the microbial populations and kinetic processes are similar in both zones.

5. Numerical simulations

Numerical simulations illustrating the interaction of physical, chemical and biological processes in field scale SVE and BV systems were conducted for a single well, axysymetric scenario depicted in Fig. 2. The domain spans both the saturated and...
unsaturated zones with a static water table at a depth of 3 m. Soil properties are homogeneous, based roughly on the Borden aquifer, and are listed in Table 5. An extraction/injection well is present in the unsaturated zone with a screened interval from 0.9–2.3 m, and an impermeable cap is placed along the ground surface to a radius of 5.6 m. The problem domain was discretized into 2300 nodes and 4480 elements, with greatest horizontal refinement near the well (0.05–1.3 m).

Boundary conditions used in the simulations are also shown in Fig. 2. No flow conditions (no gradient in pressure and concentration) were enforced along the impermeable cap, the entire bottom boundary, and the entire left boundary with the exception of the well screen segment. Constant pressure conditions were maintained along the ground surface beyond the cap radius and along the entire right boundary. Along the well screen segment, the specified constant volumetric flux was distributed over all well screen nodes at the start of each time step using a transmissibility allocation approach (Aziz and Settari, 1979). For transport solutions, a second type boundary condition was used along exit boundaries (i.e. the well screen in SVE runs and the top and right boundaries in BV runs), and third type conditions were used at all inlet boundary (i.e. the well screen in BV runs and the top and right boundaries in SVE runs).
An immobile residual NAPL composed of pure toluene is entrapped, as shown in Fig. 3, in the unsaturated zone and the saturated zone near the water table. This toluene distribution was developed by simulating the migration of a NAPL spill using an immiscible flow simulator, M-VALOR (Abriola et al., 1992). The spill scenario considered the uniform release of 200 l of toluene, over a radius of 1.5 m and a duration of 1 day. The subsequent redistribution was simulated up to 100 days, at which the time NAPL was considered to be entrapped and immobile. Chemical properties used in all simulations are listed in Table 6.

Initial conditions for the simulation of SVE and BV scenarios were developed by using the residual NAPL distribution obtained from the immiscible flow simulator and then simulating the intrinsic migration (no active remediation) and interphase partitioning of toluene constituents, including biomass development, for a period of 50 days. These initial conditions were generated prior to emplacement of the vadose well and impermeable cap. The transport parameters used in this simulation, as well as subse-

**Table 6**

<table>
<thead>
<tr>
<th>Fluid properties used in simulations</th>
<th>Toluene</th>
<th>Water</th>
<th>Nitrogen</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (g/mol)</td>
<td>98.15</td>
<td>18.0</td>
<td>28.0</td>
<td>32.0</td>
</tr>
<tr>
<td>Density (g/l)</td>
<td>998.2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Vapor pressure (atm)</td>
<td>0.0294</td>
<td>0.0231</td>
<td>–</td>
<td>0.20</td>
</tr>
<tr>
<td>Aqueous solubility (g/l)</td>
<td>0.515</td>
<td>–</td>
<td>–</td>
<td>0.009</td>
</tr>
<tr>
<td>Vapor viscosity (cPoise)</td>
<td>0.007</td>
<td>0.0097</td>
<td>0.0172</td>
<td>0.0192</td>
</tr>
<tr>
<td>Liquid viscosity (cPoise)</td>
<td>1.12</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Vapor binary diffusion coefficient (cm²/s)</td>
<td>0.077</td>
<td>0.245</td>
<td>–</td>
<td>0.085</td>
</tr>
<tr>
<td>Aqueous binary diffusion coefficient (cm²/s)</td>
<td>9.54(−6)</td>
<td>–</td>
<td>–</td>
<td>2.15(−5)</td>
</tr>
</tbody>
</table>
quent SVE/BV simulations, are listed in Table 5. These transport parameters were chosen as representative values from ranges compiled in the literature survey. Initial distributions of the organic mass, oxygen, and biomass are plotted in Fig. 3. Inspection of the figure reveals that toluene migrated radially outward from the NAPL core primarily in the gas phase by diffusion and density driven advection, with limited downward diffusion in the aqueous phase beneath the NAPL zone. Toluene partitioning into the aqueous and solid phases occurred at close to equilibrium levels. Biomass development is not observed within the NAPL zone due to substrate inhibition, growing instead adjacent to the outside edge of the NAPL zone where aqueous substrate concentrations are below the inhibition threshold. The initial microbial mass was 1.8 kg.

6. Simulation of SVE

Simulation of SVE for remediation of the soil conditions in Fig. 3 was performed by specifying a constant total fluid extraction rate of 25 cubic feet per minute (cfm) at the well. All other transport parameters were as listed in Table 5. A time series of predicted NAPL distributions in Fig. 4 shows NAPL removal progresses radially inward, and that NAPL persists within the water table and capillary fringe regions where contact with the gas stream is restricted by water table upconing. A corresponding plot of the toluene mass distribution and accumulated toluene removal is shown in Fig. 5 (Run 1). Together, plots in Figs. 4 and 5 indicate that toluene removal is greatest in the early stages of remediation, and is closely associated with the rate of NAPL removal which accounts for the majority of the total contaminant mass. In this scenario, the toluene present in the gas, aqueous and solid phases had a minor influence on mass recovery due to the selection of relatively rapid interphase mass transfer rates. Biodegradation

![Fig. 4. Progression of NAPL saturation profiles (range 0–3%) predicted from the simulation of SVE (Run 1). The contour line corresponds to the 100 ppm total toluene soil concentration and distances are in meters.](image-url)
Fig. 5. Predicted toluene mass distribution and accumulated mass removal for SVE simulations: Run 1 — base case; Run 2 — reduced extraction rate to 10 cfm; Run 3 — included dewatering (10 l/min); Run 4 — included dewatering and reduced extraction rate; Run 5 — same as Run 4 and additionally neglected substrate inhibition; Run 6 — same as Run 4 and additionally increased gas/NAPL effective mass transfer coefficient.
similarly exhibited a minor influence on mass recovery, accounting for less than 4% of the total toluene removal. Water table upconing was the controlling factor limiting full remediation. Recovery of NAPL entrapped beneath the water table is limited by aqueous diffusion to the flowing air stream. In addition, water table upconing resulted in withdrawal of about 2500 l of water through the extraction well.

Five additional SVE simulations were performed to illustrate model responses to design conditions, biological parameters, and interphase partition rates. With noted exceptions, each scenario is identical to the conditions of Run 1. The predicted toluene mass distributions and removal curves from the five additional SVE scenarios, identified as Runs 2–6, are compared in Fig. 5.

Design alternatives aimed at reducing water table upconing and increasing NAPL removal were explored in Runs 2–4. The extraction rate was reduced from 25 to 10 cfm in Run 2, resulting in a diminished rate of NAPL removal, as indicated in Fig. 5. Moreover, the effects of water table upconing were not mitigated but merely delayed, producing a minor increase in total NAPL removal of about 3 kg. The reduced extraction rate did, however, result in the benefit of nearly eliminating water extraction. Dewatering to expose the NAPL zone to the air stream was simulated in Run 3 by specifying a uniform pumping rate of 10 l/min within the water table zone between 3.5 and 3.9 m. Dewatering increased NAPL removal by about 10 kg (5.8%) over conditions in Run 1 Fig. 5, Run 3, but at the expense of increasing the total water withdrawal to 144,000 l. Here, about 5 kg (2.9%) of toluene was removed by dissolution and pumping through the dewatering well. Still, greater NAPL removal was achieved when dewatering (10 l/min) was combined with a reduced extraction rate (10 cfm) as specified in Run 4. In this scenario, the NAPL was almost entirely removed (99.8%), with only 0.35 kg remaining at the end of the simulation. Dewatering also enhanced the supply of oxygen to the capillary fringe region, increasing toluene degradation by about 5 kg (80% increase) over conditions in Run 1. Toluene degradation combined with removal by dissolution and pumping through the dewatering well accounted for 9.4% of the total removal in this simulation.

Runs 5 and 6 examined the influence of biodegradation parameters and interphase partitioning. Run 5 conditions are identical to Run 4 except here effects of substrate inhibition are ignored. A comparison of results for Runs 4 and 5 in Fig. 5 reveals little discernible differences between mass curves for the two runs. Eliminating inhibition increased toluene degradation only slightly, by less than 1 kg (7% increase) over Run 4. This effect is a consequence of the relatively small portion of the domain in which inhibition is significant. In Run 6, the gas–NAPL effective mass transfer coefficient was increased by one order of magnitude from 50 to 500 1 day⁻¹. Model predictions in Fig. 5 (Run 6) show that the gas–NAPL mass transfer rate substantially affects that rate of NAPL removal, shortening the NAPL removal time by a factor of more than one-half in comparison to all other SVE scenarios. A corresponding decrease in the maximum deviation from equilibrium partitioning (occurring adjacent to the well) occurs from about 70% in Run 1 to about 30% in Run 6. The total volume of NAPL removed also increases slightly because NAPL volatilization can occur at a greater rate prior to the influence of upconing. This effect, however, is negated somewhat by a reduction in the volume of toluene degraded due to the shortened toluene retention time.
7. Simulation of BV

Simulation of BV for remediation of soil conditions in Fig. 3 was performed by specifying a constant air injection rate of 1 cfm and employing the transport parameters in Table 5. A time sequence of simulation results is shown in Fig. 6. NAPL removal during air injection progresses radially outward, with the greatest rate of NAPL removal occurring along the pathline between the well screen and the edge of the surface cap. Similar to SVE, the NAPL persists in areas with diminished access to the gas stream — in the water table and capillary fringe region, and directly below the center of the surface cap. Fig. 6 profiles the aqueous substrate distribution and demonstrates the potential for contaminant dispersal within the subsurface as a consequence of air injection. Here, aqueous–gas partitioning and soil sorption result in the retention of toluene as it is transported by gaseous advection. In this simulation, the region of concentrated biomass initially adjacent to the NAPL zone (referred to as the ‘biofence’) does not contain the toluene flux once injection is initiated, despite the supply of oxygen. Instead, the biofence adjacent to the NAPL zone decays during the first 20 days of simulation due to substrate inhibition. Beginning at 20 days, a second region of elevated biomass concentration develops at a radius of approximately 10 m, where there is a confluence of both large oxygen concentrations and substrate concentrations below the inhibition threshold. During the subsequent 30 days of simulation, this ideal growth zone migrates upstream in response to changing NAPL and transport conditions; regions of concentrated biomass growth move radially inward and regions of biomass decay develop where oxygen or substrate become limiting.

Fig. 7 (Run 1) presents a plot of the toluene mass distribution and accumulated toluene removal over the course of this BV simulation. These results confirm that a significant quantity of toluene is redistributed into the aqueous and solid phases during the first 20 days of simulation, primarily as a consequence of radially outward flux and breakthrough of the biofence, initially adjacent to the NAPL zone. Note moreover, that the interphase partitioning rates and/or the moisture and soil holding capacity were not sufficient to fully contain the toluene plume, resulting in substantial toluene advection across the ground surface at the edge of the cap. Toluene degradation during the first 20 days is relatively small due to substrate inhibition in the biofence region initially adjacent to the NAPL zone. During this period, surface losses account for much of the reduction in toluene mass. Beginning at about 20 days, biomass development in the more favorable growth zone at a radius of approximately 10 m is sufficient to produce a noticeable increase in the rate of toluene biodegradation, and a corresponding decrease in surface flux and solid phase storage. After 50 days of simulation, surface fluxes have almost ceased, and toluene mass losses are attributable almost solely to biodegradation.

Seven additional BV simulations, identified as Runs 2–8, were performed to illustrate model responses to alternative design conditions, biological growth parameters, and interphase partition rates. With noted exceptions, each scenario is identical to the conditions of Run 1, which are those employing transport parameters in Table 5 and producing results in Fig. 6 profiles. Simulation results from all BV scenarios are compared in Fig. 7.
Fig. 6. Progression of contaminant and biomass profiles predicted from the simulation of BV (Run 1). The contour line corresponds to the 100 ppm total toluene soil concentration and distances are in meters.
Fig. 7. Predicted toluene mass distribution and accumulated mass removal for BV simulations: Run 1 — base case; Run 2 — increased cap radius 2 m; Run 3 — reduced injection rate to 0.1 cfm; Run 4 — used pulsed pumping; Run 5 — neglected substrate inhibition; Run 6 — reduced injection rate to 0.1 cfm and reduced degradation rate to 0.11 day\(^{-1}\); Run 7 — reduced gas–aqueous effective mass transfer coefficient; Run 8 — reduced aqueous–solid effective mass transfer coefficient.
Design alternatives aimed at reducing the surface flux predicted in Run 1 were considered in Runs 2–4. Increasing the radius of the impermeable cap from 5.6 to 8.8 m was tested in Run 2 as a means of enlarging the bioreaction zone and concurrently decreasing surface losses. Fig. 7 (Run 2) reveals that this strategy did produce enhanced biodegradation and reduced surface losses from levels in Run 1, however surface losses were not eliminated. Additionally, enlarging the surface cap increased contaminant redistribution and retention by the aqueous and solid phases, which resulted in substantially less toluene removal in the same time period. Such contaminant dispersal could have even more adverse impacts if contaminants are strongly sorbing and/or if desorption is the rate controlling mechanism.

The injection rate was reduced from 1.0 to 0.1 cfm in Run 3. Typical BV injection rates range up to 50 cfm for controlled flow through systems (Dupont, 1993), and injection rates ranging as high as 3–10 cfm have been reported for single well systems (Underhill et al., 1997). In general, injection rates are adjusted for site specific conditions to optimize oxygen retention time and to minimize contaminant dispersal. For the conditions of Run 3, Fig. 7 shows that reducing the injection rate enabled the biofence to contain the outward toluene flux, resulting in minimal surface loss and contaminant redistribution. These improvements occurred at the expense of substantially lengthening the total operation time. An alternative strategy, intermittent pumping, has been found in laboratory column experiments to be more efficient in terms of required injection volumes (Malina et al., 1997). Pulsed pumping was tested in Run 4. Here, a pumping schedule of air injection at 1 cfm for a period of 6 h followed by no injection for 18 h, was cycled over the course of the simulation. Results in Fig. 7 show that pulsed pumping, similar to reducing the continuous flow rate, enables the biofence to nearly contain the radially outward flux, producing almost no surface flux or contaminant redistribution. In comparison with Run 3, pulsed pumping is more efficient in terms of total operation time, but less efficient in terms of the total injection volume.

The influence of biological growth parameters was examined in Runs 5 and 6. Substrate inhibition was neglected in Run 5. Thus, in this scenario, biomass does not decay in response to elevated substrate concentration. With the influx of oxygen, favorable biomass growth conditions occur not only at the fringe of the NAPL zone, but within the NAPL zone itself. Consequently, results in Fig. 7 indicate surface losses and redistribution are substantially reduced from that of Run 1. After about 30 days of simulation, biomass development is sufficient to fully contain the toluene flux. The influence of the substrate utilization capacity on BV efficiency was examined in Run 6. Conditions in this run were identical to the reduced injection scenario of Run 3 (0.1 cfm) with the additional stipulation that the maximum substrate utilization rate was reduced by one order of magnitude (from 1.0 to 0.1 day\(^{-1}\)). Results in Fig. 7 show that toluene degradation is severely constrained by the lack of substrate utilization capacity, resulting in the inability to contain the toluene flux at the biofence. Very little degradation occurred over the course of the simulation. Recall that the toluene flux was fully contained at the higher substrate utilization rates employed in Run 3, with nearly all removal occurring by degradation.

The potential influence of interphase partitioning was examined in Run 7 in which the aqueous–gas effective mass transfer coefficient was reduced by one order of
The reduction in the mass transfer rate had the effect of reducing the substrate mass flux from the gas to the aqueous phase within the existing microbial population that was initially present adjacent to the NAPL zone. Consequently, the aqueous substrate concentration within the initial biofence region did not rise to inhibitory levels observed in Run 1, and the biofence remained relatively stationary after the start of BV. Results plotted in Fig. 7 (Run 7) show that surface losses decreased and degradation increased moderately in comparison to results from Run 1. Thus, this simulation illustrates that rate limited mass transfer can actually enhance bioavailability by avoiding substrate inhibition. Similar, but less pronounced, trends were observed from Run 8 in which the aqueous–solid effective mass transfer coefficients was reduced by two orders of magnitude for desorption processes only. Results from this scenario plotted in Fig. 7 (Run 8) show that increased contaminant retention on the solid phase during the second half of the simulation leads to slightly more toluene degradation in comparison with Run 1, which is again attributed to diminished inhibitory effects in the aqueous phase. It is anticipated that rate limited desorption would have a more substantial effect for a soil with more sorptive capacity.

8. Discussion and conclusions

This paper has presented a numerical model that advances our ability to investigate the performance of field scale SVE and BV systems by integrating processes of multiphase flow, multicomponent compositional transport with nonequilibrium interphase mass transfer, and aerobic biodegradation. Example simulations demonstrated the interplay of these processes and their potential influence on remediation efficiency and the pathways of contaminant removal.

Simulations of a single well SVE scenario revealed the following.

1. The efficiency of contaminant removal was primarily controlled by the interaction of two rates — the gas flow through the contaminated soil and the mass transfer to the gas stream.

2. The ability to engineer gas flow through regions of contaminated soil poses design and operation difficulties when contaminants are entrapped in the vicinity of the water table. Applied vacuum near the water table leads to water table upconing, which restricts contaminant mass transfer to the gas stream and diminishes removal efficiency. These effects were best mitigated by dewatering, and to a lesser extent by reducing the extraction rate.

3. The magnitude of the NAPL–gas effective mass transfer coefficient substantially influenced the rate of contaminant recovery; a one order increase in the effective mass transfer coefficient approximately doubled the NAPL recovery rate. The NAPL–gas effective mass transfer coefficient also influenced, to a lesser extent, both the quantity of NAPL recovered and the extent of biodegradation. Note that the reported and/or estimated range of NAPL–gas effective mass transfer coefficients is considerably broader than the one-order of magnitude variation examined herein. This range in reported effective mass transfer coefficients may be attributed to the potential dominance of several different mass transfer resistance mechanisms (i.e. film resistance,
contaminant occlusion, bypassing). Because of the importance of this lumped parameter, and the lack of available information on its variation, there is strong need for the development and validation of predictive mass transfer models applicable under a variety of conditions.

4. Mass losses attributed to biodegradation in the SVE scenarios were minor, about 6% or less of the total mass removal. The magnitude of biodegradation was found to be influenced by the flow rate and to a lesser extent by the biodegradation parameters.

These observations were obtained for simulations of a homogeneous soil system. Soil heterogeneities are known to strongly impact SVE efficiency, and would likely diminish the ability to generate gas flux through the contaminated zone, thereby increasing mass transfer resistance and potentially enhancing the significance of biodegradation. The MISER model provides a capability to study such effects.

Simulation of BV scenarios similarly highlight complex system dynamics and a strong relation between design parameters (injection rate, cap radius) and performance measures (degradation, surface flux, and contaminant dispersal). Results from example simulations of a single well BV scenario suggest the following.

1. Factors that affect biological growth substantially influenced model predictions. Variations in the substrate utilization rate and consideration of substrate inhibition, both within reasonable ranges, markedly influenced the quantity of toluene degradation, the extent of toluene dispersal, and the microbial growth distribution. The effects of substrate inhibition were further influenced by the rate of interphase partitioning. Nutrient addition and soil moisture content are two additional factors that may influence microbial dynamics, but were not considered in the demonstration simulations. Because of the dominant control of microbial dynamics on BV performance, work should be directed towards the quantification of Monod parameters under a variety of BV field conditions.

2. The supply of oxygen may not be the sole criterion for efficient BV performance; an optimum supply rate of both oxygen and substrate below the inhibition threshold may be required. “Optimal” substrate and oxygen supply will depend in turn on the chemical partitioning and biological growth characteristics.

3. The air injection rate was a primary control parameter for contaminant dispersal, redistribution, and surface loss. Simulations for a high flow rate (1 cfm) exhibited substantial contaminant redistribution and surface flux. At this flow rate, surface flux was a significant removal pathway, but could be reduced by factors that increased toluene retention (increased cap radius, decreased desorption rate) or increased the biodegradation (reducing effects of inhibition). A lower flow rate (0.1 cfm) eliminated toluene dispersal and redistribution with the tradeoff of substantially increasing total operation duration. Pulsed pumping at the higher injection rate improved the rate of contaminant degradation, in comparison with the performance of a continuous low flow injection, with only minor adverse effects on redistribution and surface flux.

4. Simulation results indicate that similar trends in performance measures (e.g. volume degraded and surface flux) can be observed under different remedial designs and subsurface conditions. For example, toluene degradation may be increased and surface flux decreased by increasing the cap radius, decreasing the influence of substrate inhibition, or by decreasing interphase mass transfer rate.
Comparison of simulation results from this work with those from other researchers indicates that model advances in terms of the type and representation of processes considered leads to more complicated behavior in the simulated system dynamics, which can in turn affect interpretation of system characteristics. Simulation of SVE systems conducted by Poulsen et al. (1996) showed comparable results in terms of the significant influence of nonequilibrium gas–NAPL mass transfer on removal efficiency. They further suggested that variations in the mass transfer rate influenced only the rate at which contaminants were removed but did not alter the removal pathways. In contrast, simulation results in this work indicate that mass transfer rates can affect both the quantity of NAPL removed and quantity degraded due to the added consideration of water table migration and Monod kinetics for characterization of aerobic biodegradation. These processes were also considered in BV simulations conducted by McClure and Sleep (1996), who found comparable behavior in terms of tradeoffs between flow rate, biodegradation, and contaminant spreading. Simulations in the present work indicate, however, that the incorporation of both substrate inhibition and non-equilibrium mass transfer in a modeling effort can substantially alter predictions of the quantity of contaminant degraded and the microbial growth distribution.

Together, the above comparisons illustrate that the value of numerical models depends on the type and mathematical representation of processes considered. Unfortunately, associated with increased model complexity is the requirement for greater parametric representation of individual processes. Progress in the characterization and quantification of individual processes will promote the value of numerical models for the investigation of dynamics in SVE/BV systems and for site specific remedial design.

9. Notation

\( B_{\alpha c} \) rate of moles of component \( c \) consumed by biological transformation [mol L\(^{-3}\)T\(^{-1}\)]

\( C_{\alpha} \) aqueous phase mass concentration of component \( c \) [ML\(^{-3}\)]

\( D_{\alpha \beta} \) hydrodynamic dispersion tensor of component \( c \) in phase \( \alpha \) [LT\(^{-1}\)]

\( E_{\alpha \beta} \) interphase mole transfer rate of component \( c \) to phase \( \alpha \) from all contiguous phases \( \beta \) per total volume [mol L\(^{-3}\)T\(^{-1}\)]

\( E_{\alpha \beta}^* \) interphase mass transfer rate of component \( c \) to phase \( \alpha \) from all contiguous phases \( \beta \) per total volume [ML\(^{-3}\)T\(^{-1}\)]

\( E_{\alpha}^* = \sum \Sigma \beta E_{\alpha \beta}^* \) net interphase mass transfer rate to phase \( \alpha \) from all contiguous phases \( \beta \) per total volume [ML\(^{-3}\)T\(^{-1}\)]

\( F_{\epsilon_l} \) use coefficient of component \( c \) with substrate 1 degradation [mol M\(^{-1}\)]

\( g \) gravitational acceleration vector [LT\(^{-2}\)]

\( I \) component \( c \) inhibition function

\( I_{\min}, I_{\max} \) biomass constraint functions

\( k \) intrinsic permeability tensor [L\(^2\)]

\( K_d \) biomass decay rate [T\(^{-1}\)]

\( k_{l} \) maximum substrate use rate [T\(^{-1}\)]
\[ k_{c_{\alpha}} \] relative permeability of phase $\alpha$

\[ K_{c} \] half saturation constant of component $c$

\[ K_{c_{\beta}} \] Freundlich isotherm parameter for component $c$ \( [L^3 M^{-1}]^{p_c} \)

\[ K_{a_{\beta}} \] effective mass transfer coefficient for component $c$ between the controlling phase $\alpha$ and phase $\beta \ [T^{-1}]$

\[ M_c \] molecular weight of component $c \ [M \ mol^{-1}]$

\[ n_c \] Freundlich isotherm parameter for component $c$

\[ P_{a} \] pressure of phase $\alpha \ [ML^{-1}T^{-2}]$

\[ Q_{a} \] nodal source/sinks of phase $\alpha \ [L^3T^{-1}]$

\[ S_{a} \] saturation of fluid phase $\alpha$

\[ V_{a} \] pore velocity of phase $\alpha \ [LT^{-1}]$

\[ x_{a_{c}} \] mole fraction of component $c$ in phase $\alpha$

\[ x_{a_{\beta}} \] $\alpha$ phase mole fraction of component $c$ in equilibrium with the mole fraction of $c$ in phase $\beta$

\[ x_{a_{c}}^{\min} \] minimum detectable aqueous phase mole fraction of component $c$

\[ x_{a_{c}}^{\max} \] inhibitory aqueous phase mole fraction of component $c$

\[ X \] biomass concentration \( [ML^{-3}] \)

\[ X_{\min}, X_{\max} \] minimum and maximum biomass concentration \( [ML^{-3}] \)

\[ \lambda_a = kk_{c_{\alpha}}/\mu_a \] biomass yield coefficient for substrate $l$ degradation \( [M \ mol^{-1}] \)

\[ \mu_a \] dynamic viscosity of phase $\alpha \ [ML^{-1}T^{-1}]$

\[ \omega_c \] sorbed mass of component $c$ per soil mass

\[ \phi \] porosity

\[ \rho_a \] molar density of phase $\alpha \ [mol \ L^{-3}]$

\[ \rho_s \] mass density of phase $\alpha \ [ML^{-3}]$

\[ \rho_{s} \] bulk solid phase mass density \( [ML^{-3}] \)

**Subscripts**

- \( a \) aqueous phase
- \( b \) biophase
- \( c \) component
- \( g \) gas phase
- \( l \) degradable substrate
- \( N \) nutrient
- \( N_2 \) nitrogen
- \( o \) organic phase
- \( O_2 \) oxygen
- \( s \) solid phase
- \( \alpha, \beta \) phase (aqueous, gas, organic, solid)

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